



# SILVER IN INDUSTRY

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## Preface

The logic of this book will be found in the background chapter with which it opens. The thesis is that the way to "do something for silver" is to help it find its rightful place in the family of useful metals. A group of the principal American silver producers has given very generous support, and the National Bureau of Standards and several of the eastern universities have cordially coöperated in the work towards this goal which is herein recorded.

The program comprised (1) a general survey of the field which was made in a preliminary investigation at the Bureau of Standards in 1934-5, the results of which were in part incorporated in the Bureau publication known as "C412" and which forms the nucleus of Chapter 2 of the present book; (2) a selection of the salient avenues of approach; (3) research work along these lines; and (4) the enlistment of industry in the application of developments of promise. The campaign machinery was a body of research associates, which came to be known as the American Silver Producers Research Project at the Bureau of Standards, to whose industry much of whatever has been accomplished is due. Fellows at the coöperating institutions were tied to the central office at the Bureau by circulating weekly reports and (all patent applications being barred) the public kept informed through full quarterly reports sent to all who indicated any interest.

In preparing a summary of the three years' intensive work of this second campaign, it seemed best to let it be the backbone of a book on the uses of silver, and in order to make it comprehensive, chapters on applications already well developed have been kindly contributed by those best qualified to deal with them. Several interested companies are now carrying on development work in their own laboratories and it is hoped that this book will lead others to place silver on their active list of industrial metals.

It will be seen that many minds have contributed to the investigation, and an attempt at principal acknowledgments has been made below. Special recognition should be given to the National Bureau of Standards at Washington, whose resources, both intellectual and material, have been freely drawn upon, and to its director, Dr. Lyman J. Briggs, for his tolerance towards what must have often seemed a troublesome boarder.

Finally, the writer owes a word of personal appreciation to the sponsors for the complete freedom of action afforded in his direction of this campaign.

LAWRENCE ADDICKS

Bel Air, Md.,  
March 29, 1940.

# Acknowledgments

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# Chapter 1

## The Background

BY LAWRENCE ADDICKS

The purpose of this book is to further the industrial application of silver by recording what has already been accomplished and pointing out likely lines of advance. Although matters pertaining to history, economics and production metallurgy lie outside the scope of such a definition, nevertheless a brief marshalling of certain economic data is necessary for an appreciation of the unique position in which silver stands today among the metals.

Historically silver fades into antiquity but is always associated with gold, as in the gold and silver ascribed to Abraham in Genesis as part of his wealth. That association as treasure has persisted down to the days of modern bimetallism. Gold came into use before silver for obvious reasons. Native gold is found to some degree in almost every mountain range, and as weathering proceeds the detritus becomes a placer, the stream acting as a gravity concentrator and, given enough time, probably a refiner of the unoxidizable metal. Since picking up pebbles and washing sands require but primitive tools, gold must have become available at a very early date. Silver is also found native at the grass roots, but such deposits are relatively rare. The recovery of silver from complex ores requires a metallurgical skill certainly not available in the earliest times. Herotodus is generally quoted in stories of the ancient operations, but unfortunately in addition to becoming the "father of history" he has also been accused of being the world's foremost liar. However that may be, silver and gold have lived together for several thousand years and the task of prying them apart is not an easy one. When we come to talk of silver in industry, we shall have to divorce the two completely and consider it purely as a commodity.

The law of supply and demand plays no favorites. By fixing the value of one commodity, such as gold, it is possible, assuming a genuine gold-basis currency, to throw the burden of price adjustment upon all the others; but the amount of new gold mined will also vary in relation to the value fixed—witness the recent increase in production following the lowered gold content of the world's currencies, equivalent to an increase in the price of gold. The value of silver in terms of gold has varied through the centuries, but until modern times a long-range average of about 13 to 1 has been roughly maintained while local departures from the rule have generally been downward. This ratio has not always been uni-



form throughout the world. Gold is more portable as booty and has been the more widely distributed by nature. Where trading has been difficult, silver has been relatively scarcer and more highly prized. When Japan was opened to the Occident the local ratio was found to be only 9 to 1, as against nearly 16 to 1 in America, presenting momentarily a pretty opportunity for arbitrage which was not neglected by the Americans.

It might be expected that this commercial ratio has been a measure of the relative scarcity of the two metals. Indeed some of the early fluctuations in the Mediterranean market may be traced to sudden acquisitions of gold as booty; and, curiously enough, the general weight ratio of silver to newly-mined gold during the last four and a half centuries—the only ones in which anything approaching statistics are available—is 12.8 to 1. However no such relationship is indicated in recent times, and in the face of today's commercial ratio of 100 to 1 we are confronted with a weight ratio of about 7 to 1.

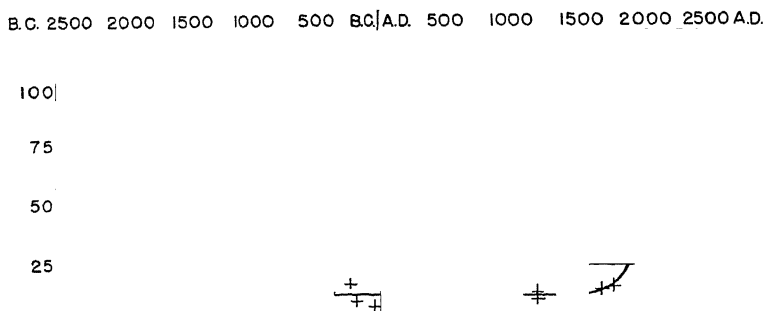


FIGURE 1. Commercial ratio of silver to gold throughout the ages.

The commercial relation is presented graphically in Figures 1 and 2, and it need hardly be pointed out that something radical has happened in the last fifty years. Beginning with the gradual demonetization of silver during the last century and the beating which 16-to-1 bimetalism took in the nineties, silver began to get out of hand; abnormal conditions during the World War restored temporary control; and since that time silver has shown increasing independence in the face of major political interference. The future is quite unpredictable, if anything is to be learned from the fate of past prophecies, but certainly present signs seem to indicate a coming free market for silver without gold entanglements.

A discussion of all the many factors involved would be far beyond the scope of this book and the competence of this commentator, but a statement of certain facts will help to point the reasons underlying the present attempt to establish silver more securely as an industrial metal.

1. Silver is a peculiarly American question. North and South America are producing 75% of the world's output. The control of nearly as great a proportion rests with United States capital alone.

2. Newly-mined silver is forced on the market. Producers do not amass stocks. Price therefore gets no protection beyond that afforded by such governments as may wish to support the value of their holdings and the minor operations of private speculators.

3. Since the first silver was taken from the ground something of the order of 18 billion ounces has been recovered. Speaking in very round numbers, one-third of this amount is today in monetary stocks, including bullion reserves; one-third is in hoards, including useful articles; one-third has been mislaid in unknown caches or wasted through use, carelessness or mishap. Therefore the equivalent of nearly 50 years' new production at the present rate can theoretically be brought into the market at a price; in considering the supply of silver we must therefore add to

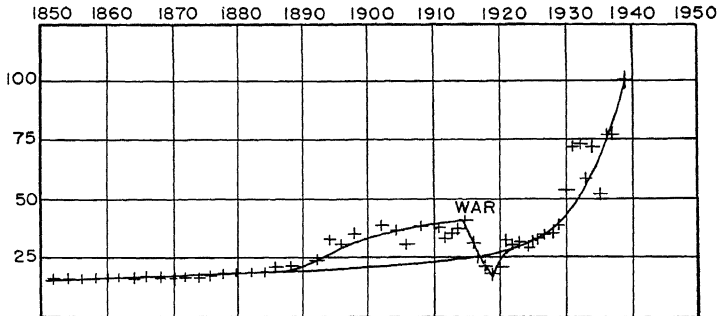


FIGURE 2. Commercial ratio of silver to gold since 1850.

current production whatever the current price will attract from such stocks.

4. With the exception of Mexico, and to a lesser degree Peru, silver considered as a commodity is of minor economic importance. The purchase of the entire world production would absorb but 0.2% of the annual income of the people of the United States. However, it plays a major role in the economy of certain geographical districts, as in the case of some sections of the western United States, and this creates political issues not for discussion here.

5. Silver occurs both native and in combination in a wide range of minerals. In many places, notably Mexico, the ore is mined primarily for its silver content and is usually treated by cyanidation, either directly or after concentration. Small amounts are also recovered by amalgamation or chloridizing; but, except in special instances, these processes have been displaced by the more efficient cyanide, in spite of the larger capital

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100

75

50

25



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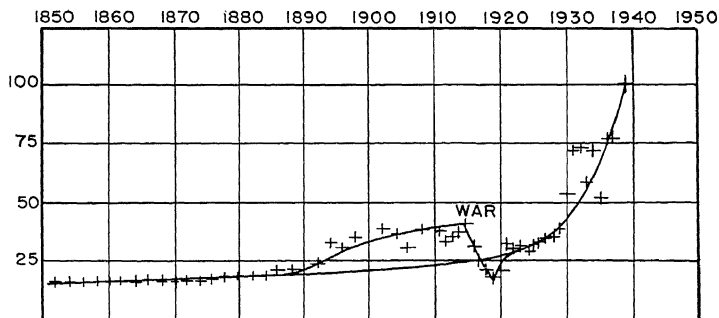


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investment required. The greater part of the world's supply, however, is produced as a by-product\* in the treatment of lead, copper, zinc (and gold) ores. The development of differential flotation has released large additional tonnages of complex ores, and silver is thus becoming increasingly a by-product metal. It is impossible to draw hard and fast lines of classification, as probably no ores have absolutely no recoverable values but silver, and there are relatively few complex deposits which depend solely on the price of silver for their operation. In general, silver production is much more dependent upon the price of lead, copper and zinc than *vice versa*. This is an intricate question, but very roughly one-third of the silver now produced may be considered as of primary origin and two-thirds by-product.

6. Now, a by-product sells in a larger market at the price set by primary material, if it is of equal quality. If, however, the market is not large enough to absorb all of it, the by-product cuts prices until it (a) drives out the primary competitor, (b) creates adequate demand at a lower price, or (c) displaces a cheaper, but for some purposes inferior, rival—in this case copper.

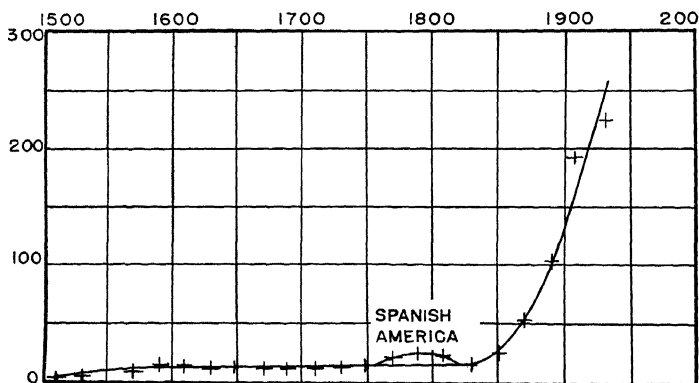


FIGURE 3. World production of silver in millions of troy ounces per year.

It is dangerous to generalize but, merely for purposes of demonstration, it may be assumed that most primary producers would lose interest in 30-cent silver and very few would answer roll-call at 25 cents an ounce. Of course, a business seldom collapses as soon as it begins to lose money, but keeps operating in hope of better times until the quick assets have been sacrificed; similarly, a mine can recast its ore reserves to become a smaller but higher-grade property. As the price drops some curtailment in marginal complex ores would also follow, so that, for

\* As used herein by-product means primary silver recovered incidentally in the production of another metal.

example, at 25-cent silver a decided drop in new production might be expected to join with whatever increase in consumption resulted from the lower price, in correcting the market situation.

When a by-product is faced with *no* market, cost of production becomes the difference between throwing it away and preparing it for sale—in this case merely that of melting fine silver sand, as all metallurgical flow-sheets carry gold and silver together until the very last step in the refining process. This is but a fraction of a cent an ounce, so that silver might conceivably displace the small equivalent tonnage of copper.

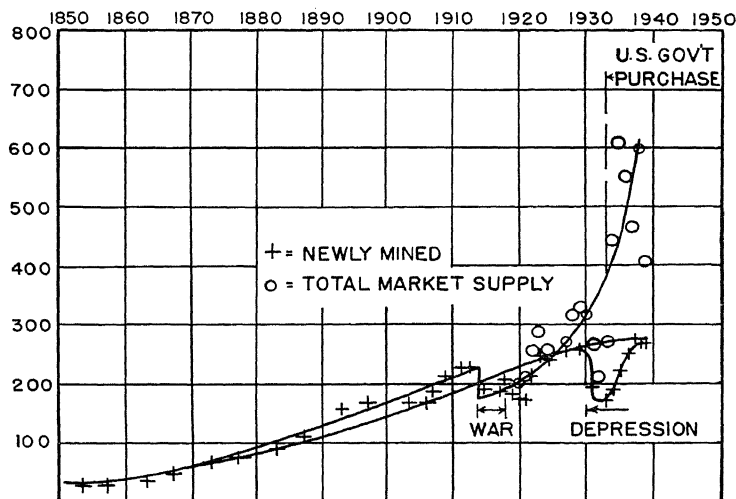


FIGURE 4. World supply of silver in millions of troy ounces per year.

7. The issues surrounding the consumptive demand for silver are no less intricate. In former times a typical year might have offered about 220 million ounces for sale; again in very round figures, 60 million each might have been expected to go into Occidental coinage, the hoards of India and the monetary system of China, the remainder, say 40 million ounces, being absorbed by industry. Today there are not many places left where silver is unlimited legal tender; indeed, in most countries silver coinage is either debased or is being replaced by tokens of nickel, bronze or stainless steel, while China has been a seller instead of a buyer. Total collapse of the market has been avoided solely by the buying operations of the United States Treasury. Industrial consumption is the only refuge, and the ultimate issue may well depend upon to what extent and how quickly the industrial uses for silver can be developed.

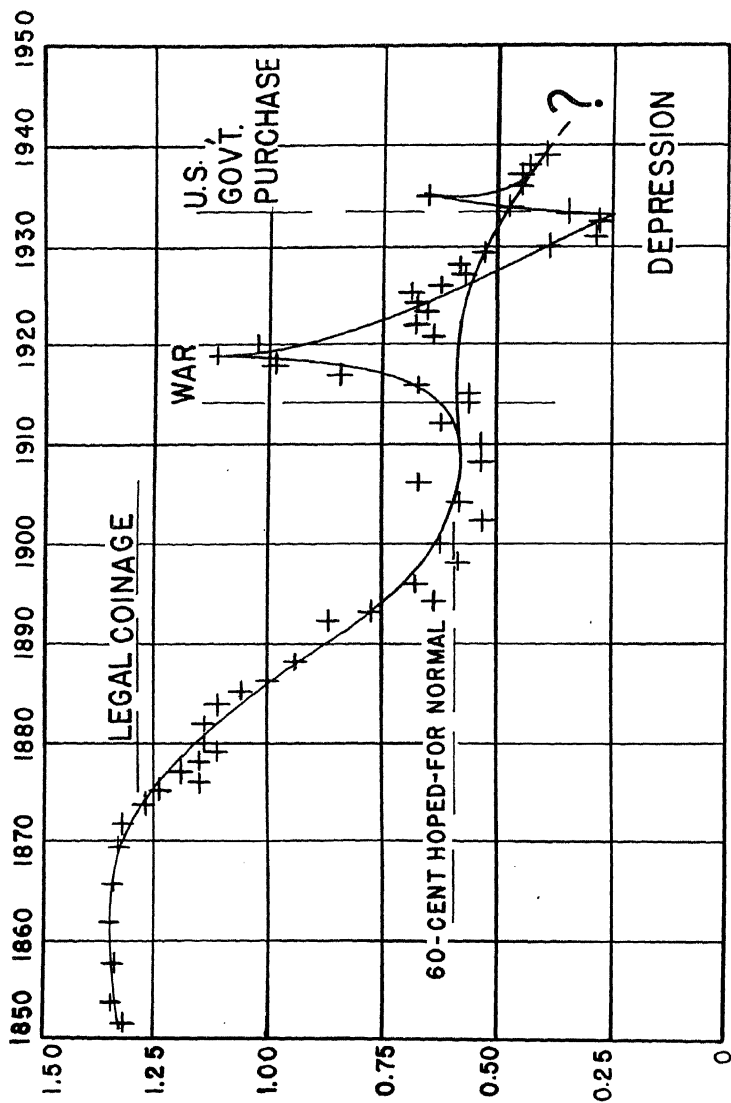


FIGURE 5. New York price of fine silver in dollars per troy ounce.

In Figures 3 to 6 the basic data for production and price are shown graphically. To bring order out of chaos it is necessary to divide the years into periods and examine each group independently. We emerge into modern times with what amounts to a bimetallic basis with a commercial ratio around 15 to 1 against gold and a small new production of silver gradually increasing. Then the demonetization of silver steadily proceeds until it effectually breaks the traditional bond to gold after the "crime of 1873." There follows a more or less free market with increasing production and falling prices, indicating a balance around 200-odd million ounces annually at 60 cents an ounce. The World War suddenly interferes and the great demand in India pushes up the price. After the

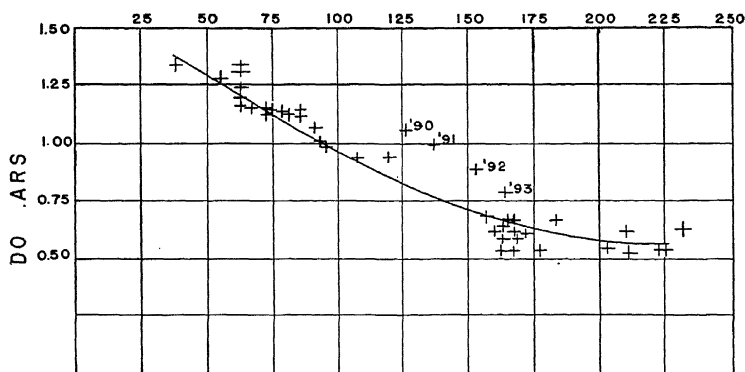


FIGURE 6. Price vs. production—1870-1913 (millions of ounces).

armistice, production regains its former trend, but the price slumps below the previous levels as demonetization and debasement proceed and India starts to unload supplies. The business depression of the thirties accentuates the difficulties and the United States steps into the breach by buying all offerings, virtually at prices of its own choosing. This suspension of natural laws has actually stimulated production and the offerings from stocks of other countries, including China, have created a world supply double that of the newly-mined product. Meanwhile, China has apparently abandoned silver as a monetary base and the Occident is showing little interest in silver coinage. The people of India, even if they remain friendly to silver, cannot be counted upon to absorb more than a minor portion of the world's production. The buying by the United States Treasury—not likely to continue indefinitely—is therefore merely postponing the day of reckoning. In this breathing spell it behooves all interested to do their utmost to create new uses.

Figure 6 is offered with considerable diffidence as showing the relationship between production and price in the period which comes nearest



to a free market. The question mark at the end of the curve in Figure 5 is the justification for this book.

In examining the graphs it should be kept in mind that (1) "fine" silver is 99.9% pure and should not be confused with London "standard," which is 92.5% silver; (2) the collection of silver statistics presents peculiar difficulties, resulting in some variations in figures from different sources; (3) statistics for the distant past are little better than intelligent guesses; (4) the points shown never cover a less period than a year and where appropriate are often averages for a period of years; (5) no account has been taken of the change in the gold content of the dollar early in 1934; (6) prices are for "foreign" silver in New York without regard to bonus on newly-mined domestic silver.

The principal sources for the data on which this chapter is based are:

Jacob's "Historical Inquiry into the Production and Consumption of the Precious Metals," Murray, London, 1831.

Blake's article on "Silver" in Johnson's "Universal Cyclopedia," Appleton, New York, 1897.

"Statistical Essay," by Soetbeer, translated by Taussig, contained in Atkinson's "Report to the President on the Present Status of Bimetallism in Europe," U. S. Government Printing Office, Washington, D. C., 1887.

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## Chapter 2

### Properties of Silver\*

By A. J. DORNBLATT †

#### INTRODUCTION

Pure silver has many interesting and some unique properties. Of all the metals, it has the whitest color, the highest electrical and thermal conductivity and the highest optical reflectivity. Only gold exceeds it in ductility and malleability. Silver possesses remarkable resistance to a wide variety of corrosive agents. It forms salts and compounds with valuable photosensitive and bactericidal properties.

In this chapter the more interesting properties of silver of high purity are reviewed. Biological and mechanical properties and those of the silver alloys are discussed separately in subsequent chapters.

#### 1. PHYSICAL PROPERTIES

##### (a) Atomic Properties

(1) *Atomic Number and Valence*.—The position of silver in the periodic arrangement of the elements is in group I and at the beginning of the last half of the second long period. Its atomic number is 47. The 47 electrons are contained in the first five quantum levels and are distributed as follows: K, 2; L, 8; M, 18; N, 18; O, 1. According to Grimm and Sommerfeld<sup>1‡</sup> the arrangement of 18 electrons in the fourth quantum level is one of great stability in the second long period of the elements. This statement agrees with the chemical behavior of silver, which almost invariably gives a univalent and colorless ion. The arrangement of the 18 electrons in quantum level 4 is too stable to be broken by chemical means.

(2) *Atomic Weight*.—The value accepted by the Committee on Atomic Weights of the International Union of Chemistry<sup>2</sup> for the atomic weight of silver is 107.880.

(3) *Isotopes*.—Aston<sup>3</sup> has reported two isotopes of silver with masses

\* The material presented is virtually a revision of the National Bureau of Standards Circular C-412, "Silver: Its Properties and Industrial Uses," by B. A. Rogers, I. C. Schoonover, and L. Jordan (1936).

† Senior Silver Research Associate, National Bureau of Standards.

‡ The superscript numbers appearing throughout this chapter relate to the numbered references in the corresponding classification of the bibliography, Appendix I, Section A, Properties of Silver.

of 107 and 109, the former being predominant, a fact which is in accord with the chemically determined atomic weight of silver.

Moussa and Laurent<sup>4</sup> have determined the periods of the radioactive isotopes of silver of atomic weight 108 and 110.

(4) *Space Lattice*.—A considerable number of determinations of the crystal structure of silver have been made. These agree in stating that the metal has the face-centered cubic lattice, and the agreement between values given for the parameter is rather satisfactory.

In summarizing the results published previous to 1931, Wyckoff<sup>5</sup> gave a lattice parameter of 4.0776A, with the last figure in doubt. Masing,<sup>6</sup> in the *Handbuch der Metallphysik*, gives 4.078A. Among later investigators, Megaw<sup>7</sup> gives the value 4.0774A for silver powder on the basis that her copper target had the wave lengths  $K\alpha_1=1.537395$  and  $K\alpha_2=1.541232A$ . Owen and Yates<sup>8</sup> arrived at the result 4.0772 at 15 °C, assuming that the radiation from their nickel target had the wave lengths  $K\alpha_1=1.65450$  and  $K\alpha_2=1.65835A$ . It seems probable, from the data presented, that the lattice parameter of silver may be safely stated to be between 4.077 and 4.078A.

Hume-Rothery, Lewin, and Reynolds<sup>9</sup> determined the lattice constant of pure silver, and give a value of  $4.0778_3 \pm 0.0001A$  at 24 °C, corresponding to 4.0773<sub>7</sub> at 18 °C. They found that for dilute solid solutions in silver, equal atomic percentages of cadmium, indium, tin, and antimony expand the space lattice of silver by amounts increasing with the valence of the solute, proportional to 2:3:4:6 respectively.

Using an x-ray camera especially designed for use at high temperature, Rothery and Reynolds<sup>10</sup> determined the lattice spacings of silver at temperatures from 19.6 °C to 943 °C with a probable accuracy of 0.0002A.

(5) *Atomic and ionic radii*.—The size of a neutral atom or an ion of silver is not constant, but depends upon its environment, its charge, the size and charge of the ion or ions with which it is combined, the crystal structure, and the type of compound formed.

For the above reasons, an accurate value of the atomic or ionic radius of silver which is applicable to all conditions, cannot be given. Values ranging between 1.40 and 1.77A have been reported for the atomic radius of silver. Bragg<sup>11</sup> from crystal measurements on metallic silver gives 1.77A for the radius. Barth and Lunde<sup>12</sup> found 1.44A, and Huggins,<sup>13</sup> following Bragg's procedure, calculated the radius to be 1.60A. For the ionic radius, Pauling,<sup>14</sup> from calculations based partly on theoretical grounds, obtained a value of 1.26A, while Goldschmidt,<sup>15</sup> from calculations based on crystal data of AgF, found 1.13A.

(6) *Allotropy*.—A number of investigators have stated, on various grounds, that silver has a number of allotropic forms, as many as four having been reported. Allard,<sup>16</sup> for example, reported finding lines in his x-ray spectrograms which indicated a noncubic form. His silver was obtained by precipitation from a silver nitrate solution by copper.

Kanecke<sup>17</sup> reported a change of form occurring between 118 and 122 °C, while others have reported allotropic modifications based on differences such as color.

It appears, however, that the evidence for an allotropic change where other factors can be completely eliminated is entirely lacking. The results of various experimenters studying specific heat have not shown any indication of such change and this fact has been commented upon by Wüst, Meuthen, and Durrer,<sup>18</sup> and in the higher temperature ranges by Jaeger, Rosenbohm, and Veenstra.<sup>19</sup> The x-ray data of Owen and Yates<sup>8</sup> for temperatures between normal room temperatures and 600 °C give no indication of such a change. It seems logical to conclude that silver which has been completely purified and reduced to the solid state will show no such effect.

(7) *Density.* (a) *Room temperature.*—The density of silver depends to some extent upon its mechanical state. For well-annealed material, either cast or worked, the measurements of Tomlinson,<sup>20</sup> Bridgman,<sup>21</sup> Honda and Shimizu,<sup>22</sup> Lowry and Parker,<sup>23</sup> Stahl,<sup>24</sup> and others indicate that the density is very close to 10.49 g/cm<sup>3</sup> (0.378 lbs./cu. in.) at room temperature. The density of cold-worked silver is distinctly less. Tomlinson states that hard-drawn silver wire has a density of 10.434 compared with 10.491 for annealed material. Honda and Shimizu give 10.44 g/cm<sup>3</sup> as the density of silver which has been hammered.

(b) *High temperature.*—Most of the measurements of the density of silver at high temperatures have been concerned with the molten material. A few values below the melting point as published by Sauerwald<sup>26</sup> are:

700 °C	.....	9.89 g/cm <sup>3</sup> .
800 °C	.....	9.80 g/cm <sup>3</sup> .
900 °C	.....	9.72 g/cm <sup>3</sup> .

Table 1 has been compiled from data published by Matuyama,<sup>25</sup> Sauerwald,<sup>26</sup> and Jouniaux,<sup>27</sup> whose results agree rather well.

Table 1.—Density of Molten Silver at Various Temperatures.

Temp. (°C)	Density (g/cm <sup>3</sup> )	Observer	Temp. (°C)	Density (g/cm <sup>3</sup> )	(Observer)
*960	9.30	Matuyama. <sup>25</sup>	1,092	9.20	Jouniaux. <sup>27</sup>
976	9.285	Do.	1,145	9.15	Do.
1,000	9.259	Do.	1,195	9.10	Do.
1,043	9.210	Do.	1,250	9.05	Do.
1,070	9.188	Do.	1,302	9.00	Do.
1,094	9.17	Sauerwald. <sup>26</sup>			

\*Extrapolated.

## (b) Thermal Properties

(1) *Change of State (Melting Point, Boiling Point, and Vapor Pressure).*—As the result of a number of investigations, the value accepted for the freezing point of silver is 960.5 °C. The freezing point of silver

defined as 960.5 °C is one of the basic fixed points of the International Temperature Scale.<sup>1</sup>

On account of the high solubility of oxygen in silver, special precautions must be taken when determining its melting point. After an extensive investigation of this question Roeser and Dahl<sup>2</sup> concluded that when a graphite crucible and a graphite cover are employed, the melting point obtained is the same as that measured in a vacuum, within the limits of error of the experiment (0.05 °C). They also investigated the depression of the freezing point resulting from the passage of air and also of oxygen through the molten bath. The maximum depression obtained in these two cases amounted to 11.2 and 22.6 °C, respectively. They, therefore, concluded that 11.2 and 22.6 °C, represent the depression of the freezing point of silver when saturated with oxygen at the prevailing pressures of approximately 149 and 760 mm of Hg, respectively.

Allen<sup>3</sup> determined the melting point of silver under mixtures of dry oxygen and nitrogen at atmospheric pressure, and obtained results, Table 2, which agree fairly well with those of Roeser and Dahl.<sup>2</sup>

Table 2.—Melting Point of Silver under Various Pressures of Oxygen.<sup>3</sup>

Oxygen content of mixture (%)	Melting point (°C)
7.8	958
20.6	951
64.0	942
97.4	938

Silver has an appreciable vapor pressure even in the solid state. Rosenhain and Ewen,<sup>4</sup> who measured the loss in weight of small pieces of silver after exposure for various periods *in vacuo* at 870 °C, concluded that fine-grained material lost weight more rapidly than coarse-grained. For example, after a 5-hour exposure a fine-grained strip of silver lost 0.0115 g/cm<sup>2</sup>, whereas a coarse-grained one lost only 0.0093 g/cm<sup>2</sup>.

Piersol<sup>5</sup> measured the loss of weight of silver filaments at various temperatures and from the data computed the vapor pressure by use of a formula. He then substituted the values of vapor pressure in Hildebrandt's vapor-pressure equation

$$\log p = \frac{0.3140 C}{T} + 7.85 + \log C,$$

where  $p$  is the pressure and  $T$  is the temperature, and calculated that  $C = 3.95$ .

The vapor pressure of silver in the liquid state is somewhat less satisfactorily determined, although the data of Greenwood<sup>6</sup> and of Ruff and Bergdahl<sup>7</sup> agree rather well, as will be seen in Table 3, which also includes the data of von Wartenberg<sup>8</sup> taken at lower temperatures.

The results in Table 3 show the good agreement between the determinations of Greenwood and of Ruff and Bergdahl for the boiling point

Table 3.—Vapor Pressure of Liquid Silver at Various Temperatures.

Temp. (°C)	Vapor pressure (mm of Hg)	Observer	Temp. (°C)	Vapor pressure (mm of Hg)	Observer
1,178	0.14	Von Wartenberg.	1,758	200	Ruff and Bergdahl.
1,316	.81	Do.	1,785	265	Greenwood.
1,435	3.9	Do.	1,810	300	Ruff and Bergdahl.
1,660	102	Ruff and Bergdahl.	1,940	744	Do.
1,660	105	Greenwood.	1,955	760	Greenwood.
1,680	116	Ruff and Bergdahl.			

of silver. Greenwood obtained a value of 1955 °C, whereas the latter experimenters gave 1950 °C. It should be noted, however, that when using nitrogen instead of hydrogen over the surface of the metal, the melting point determined by Greenwood was at least 50 °C higher. Von Wartenberg<sup>8</sup> argued strongly, on the basis of Greenwood's data with hydrogen and nitrogen and the extrapolation of his own data, that the boiling point of silver must be in the vicinity of 2100 °C. Under the circumstances, it appears inadvisable to set a definite figure for the boiling point of silver.

(2) *Thermal Conductivity*.—The thermal conductivity of silver has been measured by Jaeger and Diesselhorst,<sup>9</sup> Lees,<sup>10</sup> Bailey,<sup>11</sup> Kannuluik,<sup>12</sup> and others. Despite the difficulty of measuring this property, the results for room temperature obtained by the different observers agree rather well. Kannuluik<sup>12</sup> obtained the value  $0.999 \frac{\text{cal}}{\text{sec cm}^2 \text{ } ^\circ\text{C/cm}}$  at 0 °C on material annealed at 550 °C. Other figures for the conductivity include 1.006 at 18 °C by Jaeger and Diesselhorst, and 0.981 at 0 °C obtained by Lees<sup>10</sup> and by Kannuluik<sup>13</sup> in an earlier experiment.

Table 4, from Kannuluik,<sup>12</sup> indicates that the thermal conductivity of silver changes only moderately with temperature and very little with previous heat treatment of the metal.

Table 4.—Thermal Conductivity of Silver from -183 to 100 °C.<sup>12</sup>

Temp. (°C)	Conductivity before annealing	Cal	Conductivity after annealing	Temp. (°C)	Conductivity before annealing	Cal	Conductivity after annealing
		sec cm <sup>2</sup> °C/cm				sec cm <sup>2</sup> °C/cm	
-183	1.015		1.018	0	0.999		0.999
-78.5	1.004		1.005	100	.996		.998

Bailey's<sup>11</sup> results on the thermal conductivity of silver at temperatures up to 550 °C are given in Table 5.

Although no comment was made by Bailey concerning the condition of the specimen previous to test, the density given, 10.47 g/cm<sup>3</sup>, suggests a cold-worked material.

Bridgman has investigated the effect of tension<sup>14</sup> and of hydrostatic pressure<sup>15</sup> on the thermal conductivity of silver. According to his experiments, tension decreases the conductivity slightly. In tests at 30 °C under pressure it was possible to obtain more precise data which showed a

Table 5.—Thermal Conductivity of Silver from 100 to 550 °C.<sup>11</sup>

Temp. (°C)	Thermal conductivity Cal sec cm <sup>2</sup> °C/cm	Temp. (°C)	Thermal conductivity Cal sec cm <sup>2</sup> °C/cm
100	0.934	350	0.853
150	.917	400	.844
200	.896	450	.850
250	.880	500	.870
300	.864	550	.901

decrease in conductivity amounting to about 4.3 per cent for a pressure of 12,000 kg/cm<sup>2</sup>.

Brown<sup>16</sup> was unable to detect any change in the thermal conductivity of specimens subjected to longitudinal magnetic fields of 10,000 oersteds or to transverse fields of 8,000 oersteds. He estimated that a change larger than 0.04 per cent could have been detected by his method.

(3) *Thermal Expansion*.—The results of various investigators on the linear expansion of silver in the range between 0 and 100 °C agree fairly satisfactorily. The mean value in this interval is probably close to  $1.910 \times 10^{-5}/^{\circ}\text{C}$ , as based on the results of Keesom,<sup>17</sup> who obtained  $1.914 \times 10^{-5}$  on silver whose purity and treatment were not stated, of Buffington and Latimer,<sup>18</sup> who obtained  $1.908 \times 10^{-5}$  for the instantaneous rate at 37 °C on cold-worked material which had been cast in graphite, and of Owen and Yates,<sup>19</sup> who measured the lattice parameter of powdered silver at elevated temperatures and obtained a coefficient of  $1.908 \times 10^{-5}$ . Dorsey's<sup>20</sup> work on cast silver of density = 10.43 g/cm<sup>3</sup> covered temperatures only up to 10 °C, for which he gives a value of  $1.910 \times 10^{-5}$  for the instantaneous coefficient. As his values were increasing with rising temperature, the mean for the 0 to 100 °C interval would be appreciably higher than the figures given, but probably not so high as those of Scheel,<sup>21</sup> who published the value of  $1.968 \times 10^{-5}/^{\circ}\text{C}$  for the mean coefficient of linear expansion between 0 and 100 °C.

None of the authors mentioned appear to have considered possible changes, due to annealing effects, in this range of temperature.

Investigations of the expansion of silver at temperatures above 100 °C have been carried out by Scheel<sup>21</sup> and by Owen and Yates.<sup>19</sup> Scheel<sup>21</sup> used a sample 224 mm long, the temperature of which was maintained in a bath of sodium nitrate. As a result of his investigations, he established the equation

$$\alpha_T = 1.939 \times 10^{-5} + 2.95 \times 10^{-9} T$$

for the range from 0 to 500 °C. The x-ray investigations of Owen and Yates<sup>19</sup> led them to the expression

$$\alpha_T = 1.889 \times 10^{-5} + 3.82 \times 10^{-9} T$$

over the range from 0 to 600 °C. It will be noted that for  $T=0$  the equation of Owen and Yates is in better agreement with the results of other investigators.

Rothery and Reynolds<sup>22</sup> describe an equation which gives the coefficient of expansion of silver from the absolute zero to the melting point.

Buffington and Latimer<sup>18</sup> investigated the thermal expansion of silver down to liquid-air temperatures and found that the decrease in coefficient of expansion with temperature became more rapid as low temperatures were reached, Table 6.

Table 6.—Linear Coefficient of Thermal Expansion of Silver at Low Temperature.<sup>18</sup>

Temp. (°K)	Coefficient of thermal expansion per degree C $\times 10^{-5}$	Temp. (°K)	Coefficient of thermal expansion per degree C $\times 10^{-5}$
90	1.406	210	1.785
110	1.501	240	1.823
130	1.606	270	1.864
150	1.666	298	1.896
180	1.732	310	1.908

The values of Dorsey,<sup>20</sup> who also covered this range, are somewhat higher above 190 °K and a little lower below that temperature, but the agreement is fair for data of this kind.

Keccsom<sup>17</sup> obtained a mean value for the temperature range between  $-180$  and  $-250$  °C of  $1.037 \times 10^{-5}/^{\circ}\text{C}$ . His work indicates that the coefficient of expansion continues to decrease with temperature, probably at an increasing rate.

(4) *Specific Heat (Atomic Heat)*.—Numerous investigations of the specific heat of silver have been made. While the results are generally in fair agreement, the variation in the values of different observers is somewhat greater than can be readily accounted for by experimental errors. After a rather thorough study of the specific heat of different samples of silver, Jaeger, Rosenbohm, and Veenstra<sup>23</sup> concluded that the presence of oxygen was responsible for much of the variability in reported values. Their results, Figure 1, show the mean specific heat over various temperatures rather than specific heat as a function of

Table 7.—Specific Heat of "Oxygen-free" Silver at High Temperatures.<sup>23</sup>

Temp. (°C)	Specific heat (cal/g/°C)	Temp. (°C)	Specific heat (cal/g/°C)
0	0.0559	500	0.0622
100	.0568	600	.0635
200	.0582	700	.0646
300	.0595	800	.0659
400	.0609		

temperature. The variation, however, is approximately the same. Table 7 shows the true specific heat from 0 to 800 °C as calculated from the formula

$$C_p = 0.055401 + 0.14414 \times 10^{-4} T - 0.16216 \times 10^{-8} T^2$$

given by these authors for "oxygen-free" silver.

These results may be compared with those of Magnus and Hodler,<sup>24</sup>



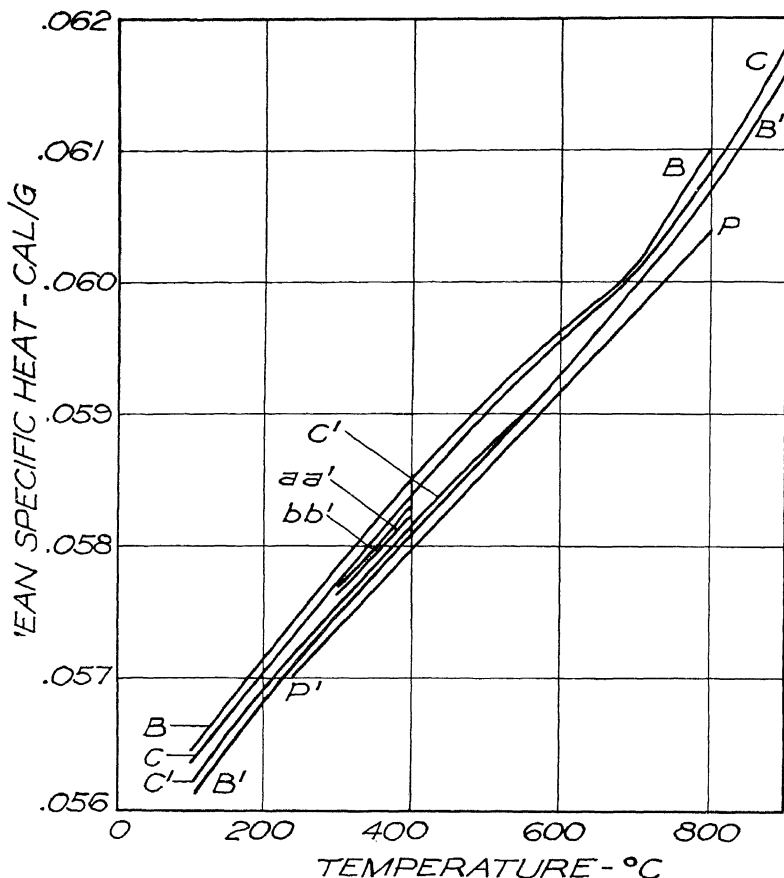


FIGURE 1. Variation of mean specific heat of silver with temperature (Jaeger, Rosenbohm, and Veenstra<sup>23</sup>).

B. Original lump fused and solidified in air.

B'. The same lump preserved for several months.

P. Electrodeposited silver.

ic heat.

respectively.

Schubel,<sup>25</sup> and Jaeger, Rosenbohm, and Bottema<sup>26</sup> as presented in Table 8, which gives both the true specific and true atomic heats.

The values obtained by Eastman, Williams, and Young<sup>27</sup> are in excellent agreement with those of Jaeger, Rosenbohm, and Bottema, Table 8.

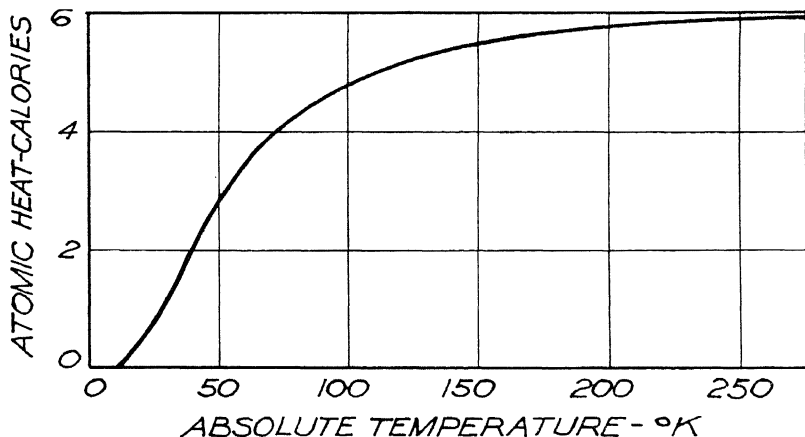
Umino<sup>28</sup> has stated that the specific heat of liquid silver is 0.0692 cal/g/°C for all temperatures from the melting point to 1300 °C. Accord-

Table 8.—Specific Heat and Atomic Heat of Silver according to Different Observers.

Temp. (°C)	Magnus, Hodler—		Schubel—		Jaeger, <i>et al.</i> —	
	Specific (cal/g/°C)	Atomic (cal/g.at./°C)	Specific (cal/g/°C)	Atomic (cal/g.at./°C)	Specific (cal/g/°C)	Atomic (cal/g.at./°C)
0	0.0560	6.047	0.0558	6.02	0.0556	6.000
100	.0568	6.129	.0563	6.08	.0571	6.167
200	.0577	6.225	.0569	6.14	.0586	6.324
400	.0598	6.460	.0596	6.43	.0621	6.609
600	.0625	6.753	.0649	7.07	.0635	6.852
800	.0658	7.102	.....	....	.0654	7.061

ingly, therefore, there is a considerable decrease in specific heat at the melting point, which is in agreement with the work of Wüst, Meuthen, and Durrer,<sup>29</sup> who found a decrease in specific heat at the melting point but an increase in specific heat with increasing temperature.

On account of its theoretical interest the change of specific heat with temperature at low temperatures has been the subject of a number of investigations. The decrease of atomic heat with temperature is well illustrated by Figure 2, from a paper by Eucken, Clusius, and Woitinek<sup>30</sup> giving their own results along with those of Griffiths and Griffiths,<sup>31</sup> Nernst,<sup>32</sup> and others. The specific heats can be obtained by dividing the values of atomic heat by 107.88.


 FIGURE 2. Atomic heat of silver at low temperatures (Eucken, Clusius and Wortinek<sup>30</sup>).

The investigation of Eucken, Clusius, and Woitinek<sup>30</sup> did not extend to temperatures below 11.4 °K. Keesom and Kok,<sup>33</sup> however, carried their work down to about 1.4 °K with the result shown in Table 9. The results of both agree well in their common range. A number of values for the atomic heat above 20 °K, from Eucken, Clusius, and Woitinek,<sup>30</sup> have been included.

Table 9.—Atomic Heat of Silver at Low Temperatures.

Temp. (°K)	Atomic heat (cal/g.at./°C)	Temp. (°K)	Atomic heat (cal/g.at./°C)	Temp. (°K)	Atomic heat (cal/g.at./°C)
1.35	0.000254	10	0.0475	60.5	3.452
2	.000626	12	.0830	79.2	4.236
3	.00157	14	.1336	103.1	4.850
4	.00303	16	.2020	124.2	5.156
				144.4	5.468
5	.00509	18	.2898	166.8	5.575
5.4	.00634	20	.3995	183.2	5.655
6	.00891	20.2	.398	205.3	5.754
7	.0151	39.8	2.013		

(5) *Heats of Fusion and Vaporization.*—Consideration of the results of a number of determinations of the heat of fusion of silver indicates that the value is about 25 cal/g. Since no account appears to have been taken of the absorption or evolution of oxygen, it is possible that heat effects other than those due simply to fusion are present. Umino<sup>28</sup> plotted the total heat of silver in both the solid and liquid states against temperature and on extrapolating both curves to the melting point of silver, obtained the result, 24.9 cal/g. Wüst, Meuthen, and Durrer<sup>29</sup> published a value of 26.02 cal/g, but as their values of specific heat are somewhat higher than those generally measured, it is possible that their value for the heat of fusion is also higher. Pionchon<sup>34</sup> in 1887 set forth 24.7 as the result of his experiments.

Direct determinations of the heat of vaporization have not been made. Estimates by Greenwood,<sup>6</sup> von Wartenberg,<sup>35</sup> and also by Jones, Langmuir, and Mackay<sup>36</sup> indicate that it is in the vicinity of 60,000 cal/g at., corresponding to 556 cal/g for boiling under 760 mm pressure. Since these estimates involve extrapolation over a considerable range in some cases, the values given should be considered as only approximate.

### (c) Electrical Properties

(1) *Resistivity.*—(a) *Room Temperature.*—The various values of the electrical resistivity of silver in the literature differ by several per cent even for material containing 99.9 per cent or more of silver. One of the most careful determinations is that of Linde,<sup>1</sup> who used silver obtained from Hilger and stated to show only a trace of calcium and no other impurities upon spectroscopic analysis. For this material, melted *in vacuo* and annealed *in vacuo*, the resistivity was found to be 1.59 microhm-cm at 20 °C for an annealing temperature of 400 °C, and to vary only by about 1 per cent for annealing temperatures ranging from 300 to 800 °C. Results obtained at the National Bureau of Standards<sup>2</sup> on silver, for which analysis showed less than 0.01 per cent of impurities and which was melted *in vacuo* and annealed *in vacuo*, did not differ significantly from this value.

(b) *Low Temperatures.*—In presenting the data on the resistance of silver at low temperatures it is convenient to express the resistance at any temperature as a fraction of the resistance of the same specimen at 0 °C.

In this way corrections for changes of dimensions are avoided, and, furthermore, the data are in their most usable form. At  $-78.5^{\circ}\text{C}$  the values obtained by various observers for well annealed material of high purity agree fairly well, but below this temperature the agreement is less satisfactory. Part of the difference may be due to the sensitiveness of resistivity to change in mechanical condition particularly at low temperatures. These data are assembled in Table 10.

Table 10.—Relative Resistivity of Silver at Low Temperatures.

Temp. (stated by observer) ( $^{\circ}\text{C}$ )	$R_t/R_0$	Reference	Temp. (stated by observer)	$R_t/R_0$	Reference
$-78$	0.684	13	$-183.6^{\circ}\text{C}$	$^{a}0.247$	27
$-78.5$	.685	24	$-192^{\circ}\text{C}$	.207	13
$-78.4$	.682	25	$20.3^{\circ}\text{K}$	$^{a}0.0089$	27
$-182.9$	.247	25	$20.4^{\circ}\text{K}$	.0100	26
$-182.8$	.235	26	$1.3^{\circ}\text{K}$	.0068	26
$-183.0$	.226	24			

<sup>a</sup>Contained 0.18 per cent of impurities.

(c) *High Temperatures*.—For the interval between  $0^{\circ}\text{C}$  and the melting point the data may again be conveniently presented as a ratio of the resistance of a given sample at the specified temperature to its resistance at  $0^{\circ}\text{C}$ . Table 11 shows the effect of increasing temperature.

Table 11.—Relative Resistivity of Silver at High Temperatures.

Temp. ( $^{\circ}\text{C}$ )	$R_t/R_0$	Reference	Temp. ( $^{\circ}\text{C}$ )	$R_t/R_0$	Reference
100	1.4098	13	500	3.19	<sup>a</sup> 3
200	1.8293	13	800	4.62	3
300	2.2626	13	900	5.14	3
400	2.710	13	960.5 (solid)	5.45	3
500	3.168	13	960.5 (liquid)	10.8	3

<sup>a</sup> Data taken from Northrup's tables or from curves in vicinity of plotted points.

Table 12 shows Northrup's<sup>3</sup> results for silver in the liquid state.

Table 12.—Approximate Resistivity of Silver in the Liquid State.<sup>3</sup>

Temp. ( $^{\circ}\text{C}$ )	Resistivity (Microhm-cm)	Temp. ( $^{\circ}\text{C}$ )	Resistivity (Microhm-cm)
960.5 (solid)	8.4	1,200	19.4
960.5	16.6	1,300	20.5
1,000	17.0	1,340	21.0
1,100	18.2		

Tsutsuni<sup>4</sup> and Matuyama<sup>5</sup> do not agree with Northrup or with each other concerning the resistivity of molten silver. The latter obtained 17.3 microhm-cm for the resistivity at the melting point, while the value obtained by the former is less than that reported by Northrup.

(d) *Effect of Impurities*.—The most complete investigation of the effect of added metals has been made by Linde<sup>1</sup> who used silver from Kahlbaum, apparently somewhat less pure than the metal which he

secured from Hilger. His results, presented graphically, are reproduced as Figures 3, 4, 5, and 6.

(e) *Effect of Annealing and Cold-Working.*—It is probable that the changes of resistance resulting upon annealing or cold-working silver are complicated by effects caused by gases which have been taken up either in melting or during annealing. A satisfactory explanation of the changes of resistance observed by Takahasi,<sup>6</sup> Credner,<sup>7</sup> Tammann and Straumanis,<sup>8</sup> and Johansson and Linde<sup>9</sup> when annealing their specimens at different temperatures in various gases or *in vacuo* is not available.

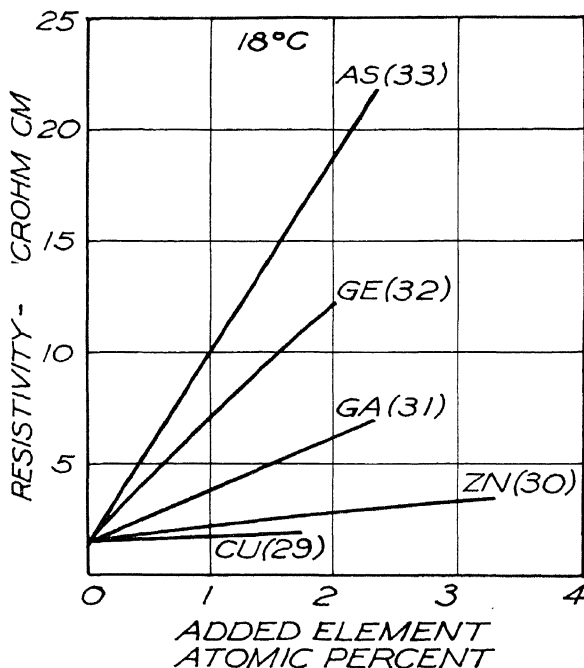


FIGURE 3. Resistivity-concentration curves for alloys of silver with the elements 29 to 33 (Linde<sup>9</sup>).

Figure 7, from Tammann and Straumanis,<sup>8</sup> shows the resistance of specimens of silver and copper wire in the cold-worked state at room temperature and the changes resulting from annealing at various temperatures in hydrogen. Some results of Credner<sup>7</sup> were included by these authors in this figure. Sieverts<sup>10</sup> measured the resistance of wires at elevated temperatures in a vacuum and then in hydrogen and observed

a marked increase in the latter case beginning at approximately 620 °C. Subsequent annealing *in vacuo* and in oxygen failed to restore the original value. According to Jellinek<sup>11</sup> the resistance of silver is increased 13.1 per cent by exposure above 500 °C to a pressure of 35 atmospheres of hydrogen.

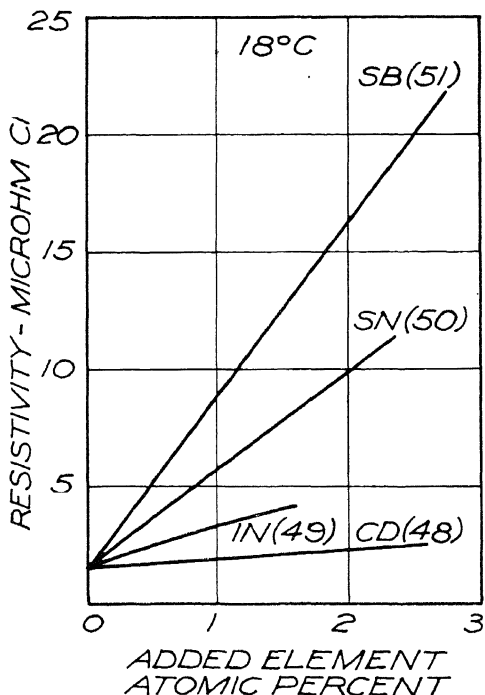


FIGURE 4.

Resistivity - concentration curves for alloys of silver with the elements 48 to 51 (Linde<sup>1</sup>).

The effect of cold-working annealed silver has been studied by Tammann and Dreyer<sup>12</sup> and Takahasi.<sup>6</sup> Both found an increase in resistance with increased reduction by drawing or rolling, but the curve of increase of resistance against percentage reduction of area obtained by Tammann and Dreyer is convex to the reduction axis, whereas that of Takahasi is concave. Tammann and Dreyer reported an increase of approximately 5 per cent in resistance for a reduction of about 90 per cent, and Takahasi, a value somewhat less.

By twisting a 2-meter length of wire 0.2 mm in diameter which had been fully annealed, Credner<sup>7</sup> found that for 150 turns there was an increase in resistance of 2.2 per cent, and this increase remained after annealing at temperatures as high as 480 °C. There appeared to be little

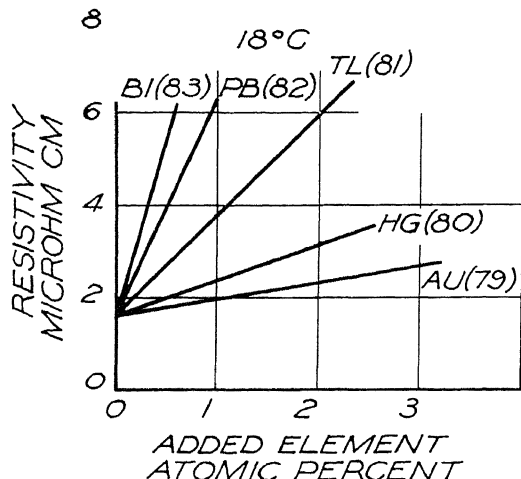


FIGURE 5.

Resistivity-concentration curves for alloys of silver with the elements 79 to 83 (Linde<sup>1</sup>).

difference in the temperature coefficient of resistance between wires twisted in this way and wires in the annealed condition.

(2) *Temperature Coefficient of Resistance.*—Measurements on the change of electrical resistance with temperature made by various observers have usually yielded values ranging from 0.00400 to 0.00410 per degree for the interval 0 to 100 °C. The earlier determinations have been tabulated by Holborn,<sup>13</sup> the highest figure given being obtained in his own investigation. Data by Wensel and Roeser<sup>14</sup> on exceptionally pure silver agree with Holborn's value, and also show very clearly that the value of this coefficient varies markedly with the purity of the mate-

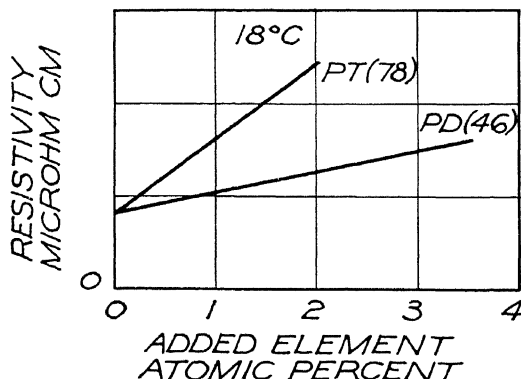


FIGURE 6.

Resistivity-concentration curves for alloys of silver with the elements 46 and 78 (Linde<sup>1</sup>).

rial. Table 13 gives the mean temperature coefficients in different temperature ranges as observed by Holborn.

Table 13.—Temperature Coefficient of Resistance over Different Temperature Intervals.<sup>13</sup>

Temperature interval (°C)	Mean coefficient	Temperature interval (°C)	Mean coefficient
-192 to -78	.004185	100 to 200	.004196
-78 to 0	.004050	200 to 300	.004344
0 to +100	.004098	300 to 400	.004487

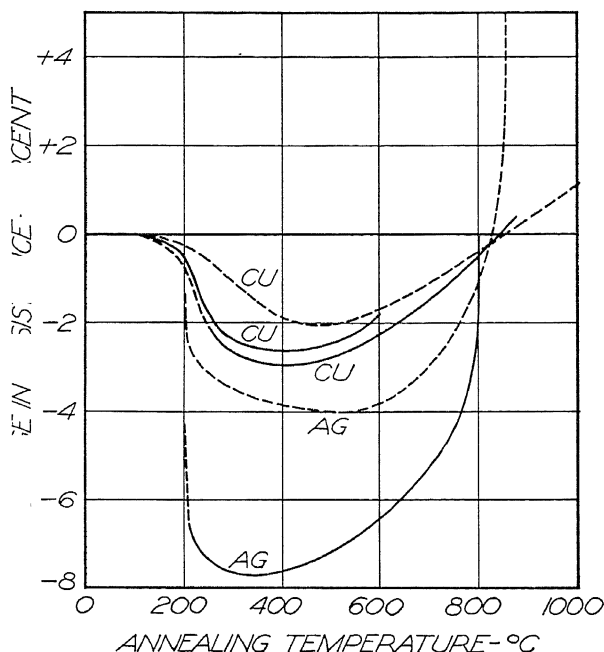


FIGURE 7. Change of resistance of silver and copper wires with annealing temperature (Tammann and Straumanis<sup>8</sup>).

Full line. From data by authors for wire reduced 90 per cent in diameter and annealed at successively higher temperatures in hydrogen for 30-minute periods.

Dashed line. From data by Credner<sup>7</sup> for silver wire reduced 42 per cent in diameter and copper wire reduced 40 per cent in diameter. Both wires annealed at successively higher temperatures in nitrogen for 3-minute periods.

The temperature coefficient is somewhat smaller for cold-worked than for annealed silver.

(3) *Change of Resistance with Pressure.*—The decrease of resistance with hydrostatic pressure up to 12,000 kg/cm<sup>2</sup> has been measured by Bridgman in the range 0 to 100 °C<sup>14</sup> and to 7,000 kg/cm<sup>2</sup> at -78.4 and



—182.9 °C.<sup>15</sup> The variation in the first case can best be represented by Table 14 calculated from Bridgman's<sup>14</sup> results. At the lower temperatures, the change of resistance with pressure is linear.

Table 14.—Relative Resistances of Silver at Various Temperatures and Pressures.<sup>14</sup>

Temperature (°C)	Resistance at the pressure indicated (kg/cm <sup>2</sup> )			
	0	4,000	8,000	12,000
0	1.000	0.986	0.974	0.960
50	1.2024	1.185	1.169	1.154
100	1.4047	1.384	1.366	1.348

At —78.4 °C the average coefficient of change of resistance with pressure over the range of 0 to 7,000 kg/cm<sup>2</sup> is  $-3.46 \times 10^{-6}$ , while at —182.9 °C it is  $-4.09 \times 10^{-6}$ .

(4) *Change of Resistance with Tension.*—Tension also has the effect of decreasing the resistance of silver as has been demonstrated by Tomlinson,<sup>16</sup> Bridgman,<sup>17</sup> and Rolnick.<sup>18</sup> Bridgman found the effect to be nearly linear up to 250 kg/cm<sup>2</sup> (3,540 lb/in<sup>2</sup>) and obtained a value of the tension (longitudinal) coefficient of resistance of  $2.86 \times 10^{-6}$  for room temperature, no correction being made for change in volume. Under loads sufficient to stress the metal beyond its elastic limit, the effect was only about 65 per cent as great. The transverse tension coefficient was only  $0.04 \times 10^{-6}$ , a quantity smaller than the limit of error of measurement.

(5) *Change of Resistance in a Magnetic Field.*—The change of resistance of silver in a magnetic field has been studied by Patterson,<sup>19</sup> Grunmach and Weidert,<sup>20</sup> and Sanders and Carman.<sup>21</sup> All agree in finding a very slight increase. The data of Sanders and Carman, which are the most complete, are reproduced in Table 15.

Table 15.—Fractional Increase in Resistance of Silver in Transverse and Longitudinal Magnetic fields<sup>21</sup> at 23 °C.

Field strength (Oersteds)	Fractional increase		Field strength (Oersteds)	Fractional increase	
	Field transverse	Field longitudinal		Field transverse	Field longitudinal
4,000	0.000004	0.0000024	12,000	0.0000356	0.0000262
6,000	.0000084	.0000052	14,000	.0000480	.0000350
8,000	.0000158	.0000106	16,000	.0000630	.0000456
10,000	.0000250	.0000183			

Patterson's data cover the range of field intensities from 17,300 to 29,200 oersteds. His data at the lower strengths are consistent with those given in Table 15. The fractional changes reported by Grunmach and Weidert were roughly 50 per cent greater than those given in Table 15.

By employing fields up to 300,000 oersteds, Kapitza<sup>22</sup> obtained very considerable increases in resistivity. At room temperature, the maximum increase amounted to about 3 per cent, and at the temperature of a mixture of solid carbon dioxide and ether, the increase was 6 per cent. The

increase was found to be 30 per cent for hard-drawn wire in liquid air and 38 per cent for annealed wire in liquid nitrogen. Figure 8 shows the fractional change of resistivity with increasing magnetic field for the lower temperatures.

(6) *Change of Resistance at Very High Current Densities.*—Measurements by Bridgman<sup>23</sup> on silver foil indicated that for a current density of 5,000,000 amp/cm<sup>2</sup> there is an apparent increase of resistance of approximately 1 per cent.

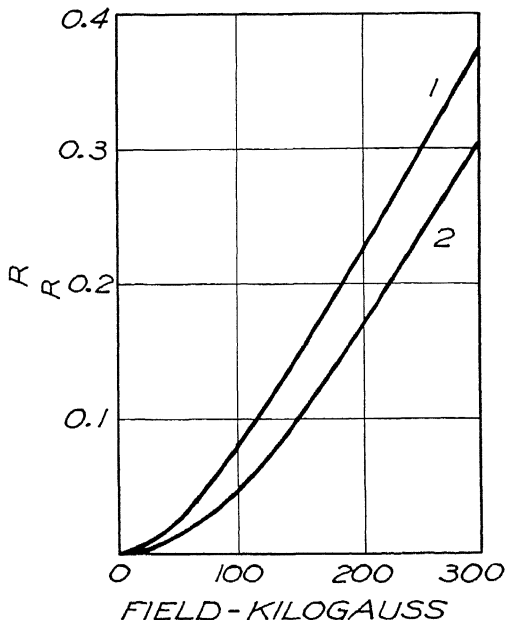
FIGURE 8.

Change of electrical resistance of silver in strong magnetic fields (Kapitza<sup>22</sup>).

Magnetic field perpendicular to current.

Curve 1. Annealed silver at temperature of liquid nitrogen.

Curve 2. Hard silver at temperature of liquid air.



#### (d) Galvanometric and Thermomagnetic Effects

(1) *Hall Effect.*—Data obtained by Smith,<sup>1</sup> Zahn,<sup>2</sup> Smith and O'Bryan,<sup>3</sup> Raethjen,<sup>4</sup> Beckman,<sup>5</sup> Ettinghausen and Nernst<sup>6</sup> and others for the value of the Hall coefficient of silver indicate that the correct value at room temperature is in the vicinity of  $-8.5 \times 10^{-4}$  cgs magnetic unit, as shown in Figure 9.

According to Smith's results the emf observed upon the introduction of a magnetic field is a linear function of the field strength when the temperature is constant. Wait<sup>7</sup> obtained a value of the same magnitude for chemically deposited films but Steinberg's<sup>8</sup> measurements on evaporated films led to the figure  $-5.2 \times 10^{-4}$ . Smith<sup>1</sup> obtained a value of  $-9.2 \times 10^{-4}$  at  $-190^\circ\text{C}$  (liquid air), while Beckman,<sup>5</sup> whose results are shown in

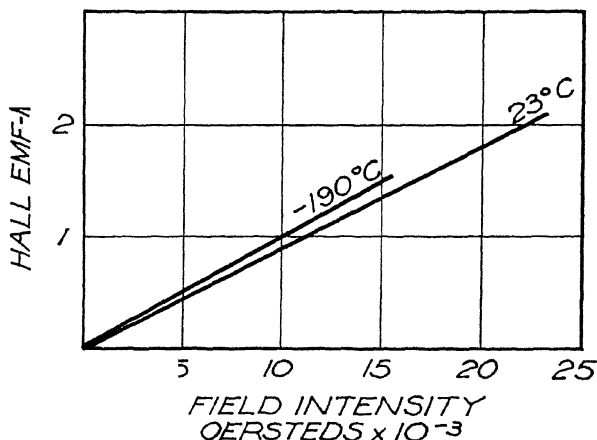


FIGURE 9. The Hall electromotive force of silver as a function of temperature and field intensity (Smith<sup>4</sup>).

Table 16, found a smaller decrease from the value given for room temperature.

Table 16.—Change of Hall Coefficient with Temperature.<sup>5</sup>

Temp. (°K)	Hall coefficient	Temp. (°K)	Hall coefficient
290	$-8.0 \times 10^{-4}$	20	$-10.15 \times 10^{-4}$
90	$-8.2 \times 10^{-4}$	14.5	$-9.9 \times 10^{-4}$

Onnes and Hof<sup>9</sup> measured the coefficient at 4.25 and 2.8 °K and reported the value  $-16 \times 10^{-4}$ .

(2) *Other Effects*.—Values of the Nernst, Ettinghausen, Righi-Leduc, and Corbino effects also show a considerable variation. In Table 17, the values obtained by various experimenters for these coefficients are given. The literature on the subject has been well analyzed and summarized in the book "Galvanometric and Thermomagnetic Effects," by L. L. Campbell. Most of the data will also be found in "International Critical Tables," volume VI, pages 414-424.

Table 17.—Various Coefficients of Galvanometric and Thermomagnetic Effects.

Effect	Value of coefficient cgs magnetic units	Observer	Reference Number
Nernst	$-4.3 \times 10^{-8}$	Zahn	
Do	$-1.8 \times 10^{-8}$	Unwin	
Ettinghausen	$-1.65 \times 10^{-9}$	Do	
Righi-Leduc	$-4.04 \times 10^{-7}$	Zahn	
Do	$-2.7 \times 10^{-7}$	Unwin	
Corbino	$-5.9 \times 10^{-7}$	Smith and O'Bryan	2
Do	$-4.9 \times 10^{-7}$	Chapman	10

<sup>a</sup> Circular plate

<sup>b</sup> Average.

## (e) Thermoelectric Effects

(1) *Thermoelectromotive Force*.—Table 18 shows the thermoelectromotive force of silver against platinum with one junction of the thermocouple at 0 °C and the other at the temperature specified. The values for temperatures above 0 °C were obtained at the National Bureau of Standards and each is the average of determinations on four samples of silver, all of which had a purity higher than 99.99 per cent. The platinum wire was the Platinum Standard, Pt 27, which is used as a reference material for all thermoelectric measurements at this Bureau. The values for temperatures below 0 °C have been computed from data on the thermoelectric power for platinum against a silver-gold alloy determined by Borelius, Keesom, Johansson, and Linde<sup>1</sup> and from data for silver against the same gold-silver alloy by the same authors.<sup>2</sup>

Table 18.—Thermoelectromotive Force of Silver against Platinum.

Temperature of variable junction (°C)	Thermoelectro- motive force (mv)	Temperature of variable junction (°C)	Thermoelectro- motive force (mv)
-200	-0.14	400	4.57
-100	-.35	500	6.36
0	0	600	8.41
100	.74	700	10.75
200	1.77	800	13.36
300	3.05	900	16.20

Positive values (not marked) indicate that current flows from silver to platinum at the cold junction. It will be observed that the data presented here for temperatures above 0 °C do not differ markedly from the results obtained by Holborn and Day.<sup>3</sup>

The values in Table 18 refer to annealed wires. The existence of a thermoelectric force between the annealed and hard-drawn portions of a single wire has been known for a long time and has been investigated for silver by Noll,<sup>4</sup> Borelius,<sup>5</sup> and Tammann and Bandel,<sup>6</sup> all of whom obtained values in the same order of magnitude. Tammann and Bandel, who used this effect as a means of determining the annealing temperature of silver, obtained a thermoelectromotive force of 46 $\mu$ v with the two junctions at 0 and 100 °C, respectively. The direction of the current is from the annealed to the worked material at the hot junction.

The effect of pressure on thermoelectromotive force was studied by Bridgman,<sup>7</sup> who measured the emf between compressed and uncompressed portions of a silver wire at various pressures up to 12,000 kg/cm<sup>2</sup>, Figure 16. The current is from uncompressed to compressed metal at the hot junction of such a couple.

(2) *Peltier Coefficient*.—Attempts have been made to determine the Peltier coefficient of a silver-copper junction by direct calorimetric methods. According to Caswell,<sup>8</sup> the coefficient has the value of -30  $\mu$ v, whereas the experiments conducted by Borelius<sup>9</sup> at 0 °C led to a value

about twice as large numerically and of the same sign. Since the total effect is small, such discrepancies are not surprising. Calculation based on data given by Borelius, Keesom, Johansson, and Linde,<sup>1</sup> yields a value of  $-90 \mu\text{v}$ . The convention used here is that the Peltier coefficient is positive when there is an absorption of heat with the current going from silver to copper. Hence, the negative sign means that heat is given off when the current crosses the junction in the direction from silver to copper.

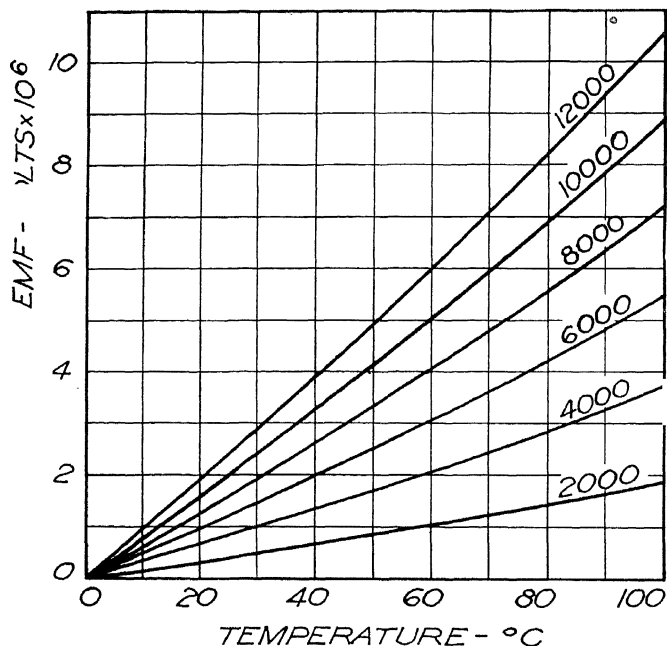


FIGURE 10. Thermal electromotive force between compressed and uncompressed silver at various temperatures (Bridgman<sup>7</sup>).

The values on the individual curves are the pressures used,  $\text{kg}/\text{cm}^2$ .

It is noteworthy that Bridgman<sup>7</sup> found a heat absorption when current flowed from the uncompressed to the compressed silver. As would be expected from the data of Figure 10, the amount of heat absorbed increased with both temperature and pressure. For temperatures of 0 and  $100^\circ\text{C}$  and a pressure of  $12,000 \text{ kg}/\text{cm}^2$ , the Peltier coefficient for uncompressed and compressed metal is  $10.6 \mu\text{v}$ .

(3) *Thomson Effect*.—A direct determination of the Thomson effect was carried out by Borelius and Gunneson,<sup>10</sup> the results of which agree

well with data calculated from measurements by Borelius, Keesom, Johansson, and Linde.<sup>1</sup> The latter data are given in Table 19.

Table 19.—Variation of the Thomson Effect with Temperature<sup>1</sup>.

Temp. (°K)	Thomson effect <sup>a</sup> ( $\mu\text{V}/^\circ\text{C}$ )	Temp. (°K)	Thomson effect <sup>a</sup> ( $\mu\text{V}/^\circ\text{C}$ )
20	1.40	180	0.72
40	.24	200	.84
60	−0.17	220	.96
80	−0.25	240	1.10
100	−0.03	260	1.20
120	.25	280	1.32
140	.44	300	1.44
160	.59		

<sup>a</sup> Positive values correspond to a heat absorption for current passing from the cold region. Pressure has the effect of increasing the Thomson heat.<sup>7</sup>

### (f) Magnetic Susceptibility

Published data on the magnetic susceptibility of silver reveal considerable variation in the values of different experimenters. A survey of the values indicates that the susceptibility is probably between  $-0.190$  and  $-0.200 \times 10^{-6}$  cgs unit.



FIGURE 11. Relation between the magnetic susceptibility of silver and density changes produced by cold-working (Honda and Shimizu<sup>7</sup>).

Owen<sup>1</sup> found that the susceptibility decreased numerically with decrease in temperature to about  $-183^\circ\text{C}$ . According to the "International Critical Tables,"<sup>2</sup> Owen's value for silver when cooled by liquid air was  $-0.16 \times 10^{-6}$ . On the other hand, de Haas and Van Alphen<sup>3</sup> were unable to find an appreciable change in susceptibility at temperatures as low as  $-259^\circ\text{C}$ . Their values between room temperature and  $-209^\circ\text{C}$  were all within the range of  $-0.188$  to  $-0.191 \times 10^{-6}$ . At lower temperatures, the accuracy was less and only the figure  $-0.19 \times 10^{-6}$  was given. Honda<sup>4</sup> measured the susceptibility at high temperatures

and found that it increased numerically with temperature. According to the "International Critical Tables," the susceptibility at 900 °C is  $-0.25 \times 10^{-6}$  and in the molten state reaches the value of  $-0.29 \times 10^{-6}$ .

Kussmann and Seeman,<sup>5</sup> Lowance and Constant,<sup>6</sup> and Honda and Shimizu<sup>7</sup> studied the effect of cold-working and found that it caused the susceptibility to drop off rapidly. Honda and Shimizu,<sup>7</sup> Figure 11, obtained a linear decrease of susceptibility with density for increasing amounts of cold-work. The effect of heating the sample slowly above its annealing temperature is shown in Figure 12. Kussmann and Seeman<sup>5</sup> expressed the belief that the change in susceptibility is not caused by the cold-working itself but by the precipitation of small amounts of iron in solid solution in the annealed metal during the plastic deformation of the metal.

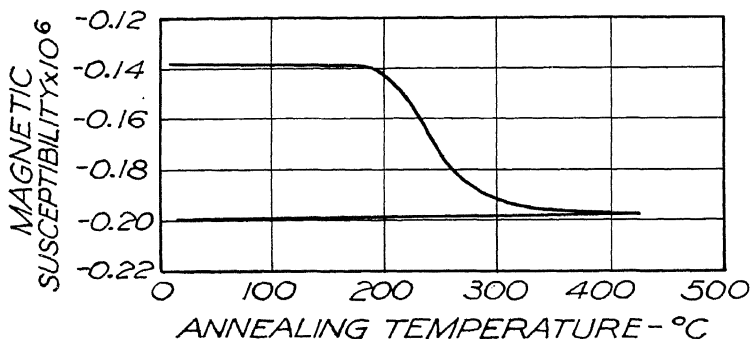


FIGURE 12. Change in the magnetic susceptibility on annealing at various temperatures (Honda and Shimizu<sup>7</sup>).

Honda<sup>8</sup> and also Vogt<sup>9</sup> found that the susceptibility increased in the negative direction with increasing field strengths, but Honda<sup>10</sup> asserts that if no ferrous material is present, the susceptibility is independent of the field strength.

### (g) Optical Properties

(1) *Reflectivity*.—Silver ranks very high among metals in reflecting power. Through the region of greatest sensitivity of the human eye, its reflectivity is of the order of 95 per cent. In the infrared region, the metal may reflect as much as 98 per cent of the radiation incident upon its surface. On the other hand, it has been found that its reflecting power diminishes with decreasing wave length and in the region of 3200Å, it falls to a minimum of less than 10 per cent.

The relation between reflectivity and wave length of the incident light, for the lower visible and near ultraviolet regions, is shown in Figure 13, based on data of Coblentz and Stair.<sup>1</sup> This shows the minimum near

3200A and also indicates the variability in the deposits employed. Some of the variations can no doubt be ascribed to differences in polish. For example, Margenau<sup>2</sup> reported that if the silver had an etched instead of a highly polished surface, the minimum of reflectivity was not so low and occurred about 20A nearer the blue end of the spectrum.

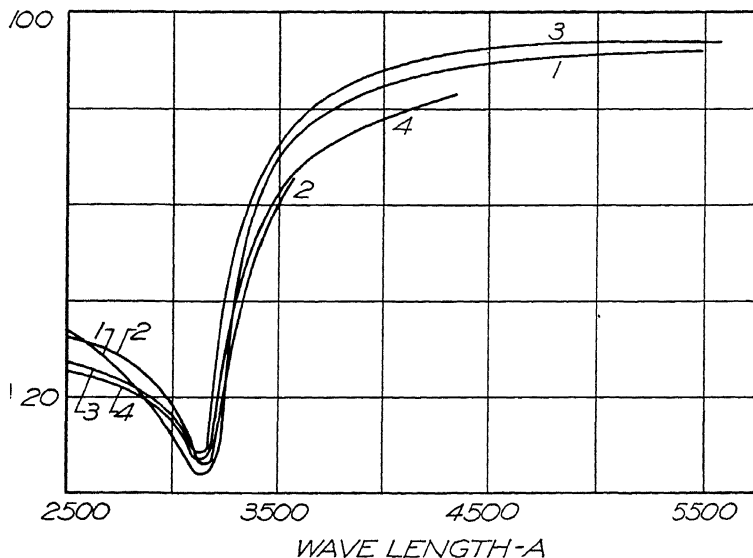


FIGURE 13. Change of reflectivity of silver with wave length (Coblentz and Stair<sup>1</sup>).

Curve 1. E. Hagen and H. Rubens (*Das Reflexionsvermögen von Metallen für ultra-violette Strahlen* Verh. d. Deutsch. Phys. Gesell., *3*, 163-176 (1901).

Curve 2. E. O. Hulburt (*The Reflecting Power of Metals in the Ultraviolet Region of the Spectrum*, *Astrophysical Journal*, *42*, 205-230 (1915).

Curve 3. Coblentz and Stair.<sup>1</sup>

Curve 4. Coblentz and Stair.<sup>1</sup>

The reflectivity of a polished silver surface is slightly reduced by annealing. Apparently the reflectivity of recrystallized silver is lower than that of the flowed surface produced by buffing and polishing. The measured reflectivity is, no doubt, influenced to some extent by the surface beneath the silver which influences the character of the silver surface in those instances where silver is deposited as a film, whether by electrodeposition, chemical reduction, or vacuum evaporation. The structure of the film is also dependent on the method whereby it was produced. Normally such factors alter the reflectivity but little; they become significant when the maximum reflectivity is in question.

The highest reflectivity values reported are apparently those of Petersen and Edwards,<sup>3</sup> who report having produced vaporized silver



films with a reflection coefficient of 99.4 per cent for a 6-volt tungsten lamp source of white light, and 98.5 per cent for light from a sodium arc.

J. W. French <sup>4</sup> reports that a specimen silvered by the Brashear process had a reflectivity of 98 per cent, whereas a specimen silvered by the Rochelle salt process had a reflectivity of only 92 per cent, and a specimen silvered by the tartaric acid process reflected only 90 per cent of the incident light.

Tests at the National Bureau of Standards have shown that good silver-plated brass specimens will reflect 95 per cent of the incident light from a tungsten lamp at 2840°K. In occasional instances somewhat higher values have been obtained.

A factor which, though probably it had no influence in producing the variations to be observed in Figure 13, is nevertheless of some interest was observed by Ebeling.<sup>5</sup> He noted that the position of the minimum of reflectivity was displaced considerably toward the red end of the spectrum when the temperature of the reflecting surface was increased from 15 to 200 °C. Information on the effect of cooling silver below room temperature, from De Selincourt,<sup>6</sup> is given in Table 20.

Table 20.—Wave-length Corresponding to Minimum Reflectivity of Silver at Various Temperatures <sup>6</sup>.

Temp. (°C)	Wave length of minimum reflectivity (A)	Temp. (°C)	Wave length of minimum reflectivity (A)
-183	3217	16	3236
- 79	* 3227	150	3247

De Selincourt also investigated the width of the minimum region and found that there was a considerable widening of the band as the temperature was increased.

Information from Coblenz <sup>7</sup> on the reflecting power of silver in the upper visible and infrared portions of the spectrum is given in Table 21.

Table 21.—Reflecting Power of Silver in the Visible and Infrared Regions.<sup>7</sup>

Wave length (A)	Reflecting power (%)	Wave length (A)	Reflecting power (%)	Wave length (A)	Reflecti power (%)
4500	88.0	9000	96.0	15000	97.6
5000	90.0	9500	96.3	17500	97.8
5500	91.5	10000	96.5	20000	97.9
6000	92.7	10500	96.7	25000	98.0
6500	93.5	11000	96.9	30000	98.0
7000	94.1	12000	97.2	35000	98.0
7500	94.7	14000	97.4	40000	98.0
8000	95.1				

(2) *Transmission*.—It is well known that silver deposited in very thin layers on glass is partly transparent. Houston and Moore <sup>8</sup> found that as the wave length is decreased from 7000 to 4600A, the amount of light reflected by a thin layer of silver decreased while that transmitted

increased. It is also true, however, that very thin silver foil, *e.g.*, 3 to  $5 \times 10^{-6}$  cm in thickness, is not entirely opaque. Swamy<sup>9</sup> has mentioned the blue color of silver when viewed by transmitted light. The transmission band which occurs in the region of short wave lengths was found by Rayleigh<sup>10</sup> to change in position when the silver was cooled to the temperature of liquid air. The effect was studied in more detail by McLennan, Smith, and Wilhelm<sup>11</sup> who obtained the results shown in Table 22.

Table 22.—Change of the Wave-length of Maximum Transmission with Temperature of Silver Sheet<sup>11</sup>.

Temp. (°C)	Wave length of maximum transmission (Å)
20	3243
- 182	3212
- 251	3200
- 269	3198

(3) *Emissivity*.—The emissivity of silver for a wave length of 6500Å is very low at all temperatures, a fact which would be anticipated from a knowledge of its high reflecting power. In general, experimenters have determined the relative emissivity, that is, the ratio of the intensity of the radiation in the given wave length to that produced by a black body at the same temperature.

Bidwell<sup>13</sup> measured the actual temperature and the apparent temperature (temperature at which a black body would radiate with the same intensity at the given wave length) of silver from about 700 to 1800 °C and found a linear relationship for a wave length of about 6600Å. For a true temperature of 700 °C, the apparent temperature was about 595 °C and at 1800 °C, the apparent temperature was about 1380 °C. He obtained a value of 0.055 for the relative emissivity at the low temperatures and a very slightly higher value at high temperatures. The relative emissivity was nearly constant over the entire range and no discontinuity was observed at the melting point.

Burgess and Waltenberg<sup>14</sup> obtained a somewhat higher value of relative emissivity at 940 °C (0.044) than at 980 °C (0.072) which suggested a higher emissivity in the liquid state. These experimenters used a filter transmitting an average wave length of 6500Å, measured the actual and apparent temperatures of a minute amount of silver placed on a heated platinum strip, and calculated the relative emissivity.

(4) *Photoelectric Properties*.—The photosensitivity of silver salts, such as the halides, is the basis upon which the photographic industry has been built. Photographic application of silver is discussed in Chapter 18, and it is the purpose here to consider the response of silver to radiation and the use of silver in photoelectric and fluorescent tubes.

For television purposes, the photosensitive surface most widely used today, according to Zworykin and Morton,<sup>15</sup> is the so-called cesiated silver surface. A mosaic of microscopic silver particles on a mica sheet

is employed in the iconoscope used in transforming a visual image into electrical impulses. The sensitized surface emits electrons when struck by radiant energy or photons. The preparation and microstructure of the mosaic photoemitter is described by Fink.<sup>16</sup> According to Hughes and DuBridge,<sup>17</sup> the photoelectric work function of silver is 4.73 and the thermionic work function is 4.08. Huxford<sup>18</sup> discusses the Townsend ionization coefficient in cesium-silver-oxygen photo-tubes filled with argon.

(5) *Miscellaneous Optical Properties*.—Silver acts as an activator for phosphors of the zinc-cadmium sulfide type. As little as one part per million of silver affects the emission curve, according to the data of Leverenz and Seitz.<sup>19</sup> Compounds of silver are useful in the manufacture of luminous material and intensifying screens for x-rays.\* Wehl<sup>20</sup> states that glass containing about two-tenths per cent of silver, in a properly activated condition, fluoresces with the production of a very white light.

## 2. CHEMICAL PROPERTIES

### (a) Electrochemical

(1) *Electrolytic Solution Potential*.—In the electrochemical series, silver lies below hydrogen together with copper, thallium, mercury, and gold. Silver is electropositive to such metals as copper, tin, and lead. It is more resistant to oxidation than these metals and therefore more resistant to corrosion under oxidizing conditions. Silver is slightly less electropositive than gold and more readily oxidized than this metal, but because of the relatively high positive electrolytic solution potential it may be placed on the borderline of that group of metals called "noble." The standard electrolytic solution potential  $\text{Ag}^+ + e = \text{Ag(s)}$  as given in "International Critical Tables"<sup>1</sup> is +0.7978 volt at 25 °C.

(2) *Hydrogen Overvoltage*.—The hydrogen overvoltage at a silver surface in  $2N \text{ H}_2\text{SO}_4$  at 25 °C as given in "International Critical Tables"<sup>2</sup> varies with the current density as shown in Table 23.

Table 23.—Hydrogen Overvoltage on Silver in  $2N \text{ H}_2\text{SO}_4$  at 25 °C.<sup>1</sup>

Current density (ma/cm <sup>2</sup> )	Overvoltage (volts)	Current density (ma/cm <sup>2</sup> )	Overvoltage (volts)
0.1	.298	100.0	0.875
1.0	.475	200.0	.938
2.0	.579	500.0	1.030
5.0	.692	1000.0	1.089
10.0	.762	1500.0	1.084
50.0	.830		

### (b) Corrosion

The published technical information on the corrosion resistance of silver is scanty, although articles of a trade nature, especially on the use of silver in the construction of chemical plants, are numerous. Most

\* British Patent 499,607.

of these articles do not include experimental information, and many of those presenting data merely repeat what has already appeared elsewhere.

In many instances, silver equipment is being used for purposes which the chemical manufacturer prefers not to make known. For this reason, corrosion data based on commercial experience are seldom made public. Nevertheless, a wider knowledge of successful applications of silver will benefit the chemical industry, point the way to products of higher quality, and reduce the difficulties caused by corrosion. This is especially pertinent at the present time when the price of silver is low, and advances in silver technology have increased the range of sizes and the variety of commercially available forms.

One can conveniently ascertain what is known regarding the resistance of silver to corrosion by specific agents by consulting Chapter 15, which summarizes the corrosion data obtained at Lehigh University, under the sponsorship of the Silver Project. The reader's attention is also invited to the bibliography, in which are many references pertaining to the corrosion of silver and its alloys.

### (c) Catalytic Properties

The catalytic properties of silver and its salts have been extensively investigated in recent years, and silver and some of its compounds are known to function as catalysts in a wide variety of reactions. This matter is discussed in Chapter 14, and a list of references will be found in the bibliography.

### (d) Chemical Analysis

Hillebrand and Lundell<sup>1</sup> have discussed in some detail the standard methods for treating various ores of silver for chemical analysis. This reference book should be consulted for detailed procedures.

In the ordinary scheme of analysis, solution of the sulfide-arsenide type of silver ores is best obtained by digesting the ore with nitric acid followed by a sodium carbonate fusion, after which the melt is treated with water, then with nitric acid. The silver from these solutions is removed as a sulfide by hydrogen sulfide following the removal of the silica by dehydration with nitric or sulfuric acid. The silver sulfide is dissolved in nitric acid and the silver determined by one of the following procedures: (A) gravimetric; (B) volumetric; or (C) electrometric.

In the gravimetric method the silver is precipitated from a dilute nitric acid solution by dilute hydrochloric acid, dried at 280 °C, and weighed as silver chloride. For very high accuracy, the sample can be transferred to a porcelain crucible and fused at about 455 °C.

## 3. FRICTIONAL PROPERTIES

The friction of silver against itself and other metals *in vacuo* has been studied by Shaw and Leavey.<sup>1</sup> At room temperature, the coefficient of friction of silver against itself is about 2.6, which is relatively high

for the metals investigated by these authors. This is consistent with the tendency of silver to weld to silver, as discussed in Chapter 6, and with the absence of protective oxide films such as are usually present on base metals and which are known to affect materially their frictional properties and wear resistance.<sup>2</sup> Shaw and Leavey found that the coefficient of friction of silver against iron is about 0.3, the lowest of any combination tested.

Tichvinsky<sup>3</sup> described bearing tests performed in the region of semi-fluid or boundary lubrication. For a chromium-plated journal operated in different bearings, the silver bearing showed a lower value of starting friction than was the case for a tin-base babbitt, a plastic bronze, and a leaded tin-bronze bearing.

Dayton<sup>4, 5</sup> has conducted an extensive investigation of the characteristics of silver bearings. He reports that steel-backed silver bearings of high purity have excellent load-carrying ability and are being used for heavily-loaded aviation engine crankshaft bearings. This application of silver is discussed at length in Chapter 8. The frictional properties of silver are improved by a small percentage of lead, and Faust<sup>6</sup> discusses the preparation of suitable lead-silver bearings by electrodeposition.

The authors have been advised \* that silver-faced steel is extremely resistant to galling or scoring when placed in sliding contact with a steel surface. Silver, or a silver-cadmium alloy, has been found effective in reducing the galling of K-monel.

\*E. A. Ryder, Research Engineer, Pratt and Whitney Aircraft Div., United Aircraft Corp., E. Hartford, Conn., Personal communication.

# Chapter 3

## Binary Silver Alloys

By A. J. DORNBLATT

### I. SCOPE OF SILVER PROJECT METALLURGICAL PROGRAM

#### 1. General

The industrial uses of unalloyed silver are naturally based on some unusual property, or some superior combination of properties for which the user is willing to pay the necessary premium. The largest uses of the pure metal *per se* are based on three characteristics: (a) corrosion-resistance of a superior order; (b) unsurpassed electrical conductivity and the ability to maintain low resistance at contact faces; and (c) the ability to reflect almost all radiation in the spectral region to which the eye is sensitive, with practically no selective absorption. These characteristics, respectively, account for the use of metallic silver for construction of chemical equipment, in electrical contacts and switch gear, and for reflectors and decorative coatings.

In all three fields, pure silver is deficient in certain attributes. It is a mechanically soft, weak metal, easily scratched or abraded, and it tarnishes readily in urban or industrial atmospheres. Obviously there would be wider use of the metal if it possessed the aforementioned qualities, plus greater mechanical strength and tarnish resistance.

Metallurgical theory indicates that silver can be strengthened without commensurate loss in resistance to corrosion, electrical conductivity, and workability. Silver-rich homogeneous alloys of the solid solution type may be expected to exhibit greater strength and hardness without substantial loss in resistance to corrosion, but with material loss in conductivity. Polyphase alloys rich in silver will probably be more subject to corrosion as a consequence of selective attack on the less noble phase or as a result of galvanic action between the dissimilar phases. If the second phase is present in slight amount and can be largely precipitated from solid solution, the conductivity may not be greatly reduced, although strength, hardness and abrasion resistance may be materially improved. The investigation of silver alloys from this viewpoint is bound to be fruitful and has received attention by the Project.

One other approach to developing industrial alloys containing silver has been considered. This is the possibility of improving base metal alloys by the addition of a relatively small percentage of silver. Perhaps the best known instance of improvement of this kind is the effect of a few hundredths per cent of silver in raising the recrystallization

temperature of copper. For certain applications involving heating cold-rolled or drawn copper, this improvement justifies the additional cost of the silver. Very little information is found in the technical literature on the use of silver as a minor alloying element, although the patent literature (see Appendix II, Section 2) indicates several commercial applications of some importance.

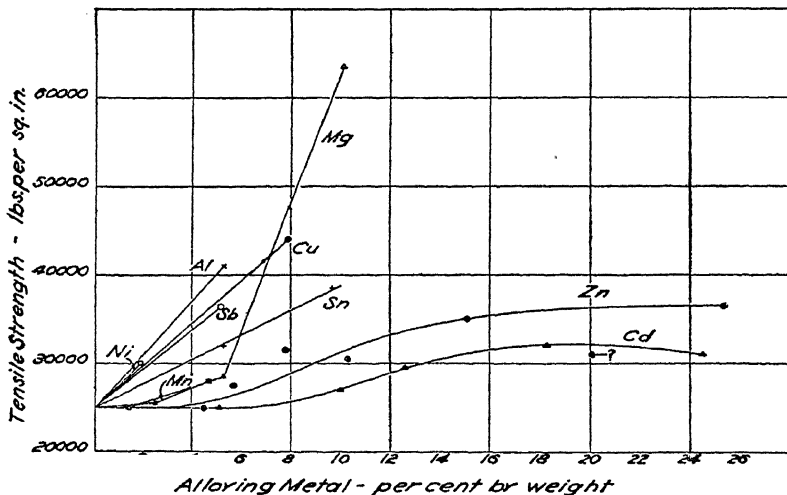


FIGURE 1. Effect of alloying metals on the tensile strength of silver in binary alloys (Jordan, Grenell, and Herschman).

## 2. Previous Work<sup>†</sup>

About 1924, Jordan, Grenell and Herschman<sup>††</sup> undertook a study of tarnish-resisting silver alloys. Their conclusions with respect to the relative tarnishability of the alloys investigated are reviewed in

<sup>†</sup>The results of metallurgical interest obtained by the various investigators under Project sponsorship are detailed in the following publications filed in the National Bureau of Standards library:

B. A. Rogers, I. C. Schoonover, and L. Jordan. Silver: its properties and industrial uses. Cir. C 412, N. B. Stds. (1936).

B. A. Rogers, and I. C. Schoonover. Progress Reports, First Silver Research Campaign (1934). N. B. Stds. Library.

A. J. Dornblatt, et al. Progress Reports, National Bureau of Standards Silver Project staff (1937-1940). N. B. Stds. Library.

B. S. Old. Progress Reports, Mass. Inst. of Tech. Silver Research (1938). N. B. Stds. Library.

V. S. de Marchi. Progress Reports, Columbia Univ. Silver Research (1938). N. B. Stds. Library.

J. M. Thomas. Progress Reports, Lehigh Univ. Silver Research (1939-1940). N. B. Stds. Library.

<sup>††</sup>L. Jordan, L. H. Grenell, and H. K. Herschman. Tarnish resisting silver alloys. Tech. Paper No. 348. N. B. Stds. (1927) [also, *ibid*, Trans. A. I. M. M. E. 76a, 460-480 (1927)].

Chapter 15. In general, it can be stated that alloys more tarnish-resistant than sterling silver were developed, but none that possessed the color and workability of sterling were sufficiently tarnish-proof to warrant commercial exploitation. These investigators determined the physical properties of a number of binary silver alloys, as summarized in Figure 1.

Schoonover and Rogers, in 1934, undertook a survey of possible industrial uses for silver and included some metallurgical studies on several binary silver alloys, which are reviewed elsewhere in this chapter.

### 3. Present Work

When the Silver Project was established on a more extensive scale in 1937, a metallurgical program was mapped out for the purpose of exploring the alloy field. This work centered at the National Bureau of Standards, where the facilities of the Metallurgical Division were made available. Between 1937 and 1940, ingots of approximately 250 different alloy compositions were prepared, fabricated, and subjected to physical tests and metallographic examination. Most of the alloys were prepared during the first year's work, and were examined by B. S. Old, research fellow at Massachusetts Institute of Technology, for their response to heat treatment, and by V. S. de Marchi, research fellow at Columbia University, for their resistance to corrosion by intermittent immersion in a three per cent sodium chloride solution. Meanwhile, the alloys were being studied at the National Bureau of Standards to determine their tensile properties, annealing temperature, electrical conductivity, hardness, and special characteristics. After a lapse of nearly a year in the metallurgical program, while the container program was receiving major attention, the metallurgical studies were resumed at the National Bureau of Standards and corrosion studies were made by J. M. Thomas at Lehigh University.

The metallurgical program adopted had two objectives, as outlined originally in the Second Progress Report dated May 24, 1937, as follows:

- I. Improvement of Base Metal Alloys by Silver Additions.
  - A. Where the high thermal or electrical conductivity of the parent metal (copper, aluminum, or magnesium) is to be retained to an important extent and it is desired to
    - a. Increase strength and hardness,
    - b. Increase strength at high temperature,
    - c. Otherwise improve the alloy (casting characteristics, etc.)

Typical possible applications: cylinder heads and pistons of internal combustion engines; electrical conductors, windings, switch parts, welding electrode tips.

- B. Where improvement is sought by additions of small amounts of silver to established commercial alloy types to
  - a. Improve corrosion resistance,



- b. Improve physical properties: raise annealing temperature, improve machinability, ability to take high polish, soundness of castings and welds,
- c. Confer special properties: optical reflectivity, bearing qualities, joining qualities, electrical qualities.

Typical possible applications: insoluble anodes for electrolytic processes; chemical equipment construction; storage battery grids; bearings (Cd); solders; condenser tubing; hardware; welding rod.

## II. Development of Improved Silver-Rich Alloys exhibiting

- a. Greater strength, hardness and abrasion resistance,
- b. Greater resistance to corrosion (including, but not restricted to sulfide corrosion),
- c. Desirable electrical characteristics, *e. g.*, high conductivity plus greater strength and wear resistance,
- d. Special characteristics such as
  - 1. High optical reflectivity plus resistance to abrasion and tarnish,
  - 2. Low coefficient of friction plus high thermal conductivity and "wetting" properties, a combination of interest as a possible antifrictional material,
  - 3. Adaptability for electric welding of other metals,

Typical possible applications:

Constructional material, either solid or duplex, for applications requiring corrosion resistance with greater hardness and strength at lower cost and lighter weight than now is obtainable with pure silver; silverware; ornamental identification discs; electrical contacts; special windings, commutators; switches; welding electrode tips; head-light reflectors, bearings and shims for high-speed engines.

It is of interest to note that, either in its own work or in information obtained by a study of the technical and patent literature, or through personal communication with industrial research workers, the Project has subsequently learned of an alloy containing silver meeting specifications for practically all of the possible applications cited.

The greater part of the work undertaken to note the effect of small additions of silver on common engineering alloys is discussed in Chapter 4, devoted to ternary and complex alloys. The binary alloys prepared and studied by the project staff are listed in Table 1, and the results obtained are discussed under the appropriate binary alloy system. A literature search has been made and a comprehensive bibliography<sup>†</sup> on the alloys of silver is given in Section B of Appendix I. The primary

<sup>†</sup>Section B of the Bibliography is classified according to the convention adopted in the text of this chapter. The alloy systems are alphabetically arranged and numbered from 1. Aluminum-Silver to 47. Zirconium-Silver. References cited, indicated by superscript numbers in the text, are identified by corresponding marginal notations in the bibliography on the particular alloy system.

Table 1.—Composition\* of Binary Alloys Studied.

<i>Aluminum</i>		<i>Magnesium</i>	
Ag	Al	Ag	Mg
Trace	99.82	Rem.	3.08
0.12	Rem.	Rem.	6.13
1.30	Rem.		
7.00	Rem.		
10.00	Rem.		
71.00	Rem.		
87.50	Rem.		
89.50	Rem.		
92.00	Rem.		
94.90	Rem.		
97.50	Rem.		
<i>Antimony</i>		<i>Manganese</i>	
Ag	Sb	Ag	Mn
Rem.	46.24	99.25	0.75
Rem.	23.66	Rem.	2.63
Rem.	20.35	Rem.	4.06
Rem.	11.84	Rem.	6.62
Rem.	6.76	Rem.	16.16
Rem.	5.80	Rem.	17.92
		Rem.	19.82
		0.77	Rem.
<i>Arsenic</i>		<i>Nickel</i>	
Ag	As	Ag	Ni
Rem.	2.23	Rem.	0.10
<i>Copper</i>		<i>Silicon</i>	
Ag	Cu	Ag	Si
0.002	99.951	Rem.	0.25
0.08	Rem.	Rem.	0.31
1.09	Rem.	Rem.	0.78
		Rem.	0.87
		Rem.	1.47
		Rem.	1.53
		Rem.	1.63
		Rem.	2.56
		Rem.	2.57
		Rem.	3.89
		Rem.	4.43
		Rem.	6.09
<i>Lead</i>		<i>Zinc</i>	
Ag	Pb	Zn	Ag
	99.995	Rem.	0.003
2.32	Rem.	Rem.	0.098
4.68	Rem.	Rem.	0.99
5.00	Rem.	Rem.	1.01
60.48	Rem.	Rem.	2.18
0.60	Rem. <sup>1</sup>	Rem.	4.74
2.38	Rem. <sup>1</sup>	Rem.	6.63
3.78	Rem. <sup>1</sup>	Rem.	8.69
5.14	Rem. <sup>1</sup>	Rem.	10.77
6.88	Rem. <sup>1</sup>	Rem.	15.97
		Rem.	21.22
		Rem.	31.60

\* Rem. indicates remainder, by difference.

<sup>1</sup> 0.44% tin .04 Sb, .04 Bi.

motive in studying the silver-rich alloys was to obtain a mechanically superior metal retaining the desirable characteristics of the parent element, silver. In particular, there is a definite need in the synthetic chemical industry for a metal possessing the corrosion-resistance of silver, but with superior mechanical properties at elevated temperature. The physical properties of fine silver (99.9 per cent grade) can be materially improved by cold working, but this improvement does not

persist, owing to annealing effects produced by moderately elevated temperature. For this reason, attention was devoted to obtaining annealing temperature data on the silver-rich alloys. The resistance of some of these alloys to corrosion is being studied at Lehigh, and at the Bureau their resistance to tarnish was observed as a matter of routine. The binary alloys of tin, lead, copper, and zinc with small amounts of silver were studied for special reasons discussed later.

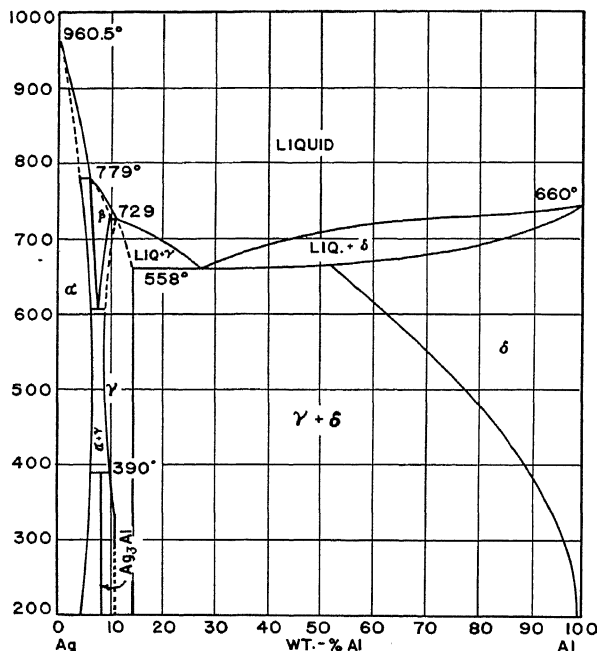


FIGURE 2. Aluminum-silver constitutional diagram.

Hoar and Rowntree: *J. Inst. Metals*, **46**, 119 (1931).

Westren and Bradley: *Phil. Mag.*, **6**, 280 (1928).

Hansen: *Z. Metallkunde*, **20**, 217 (1928).

Petrenko: *J. anorg. Chem.*, **46**, 49 (1905).

## II. CONSTITUTION, PROPERTIES AND APPLICATIONS OF BINARY ALLOYS

### 1. Aluminum-Silver

#### (a) Constitution

Figure 2 is the constitutional diagram for aluminum-silver alloys, prepared by the Project, based on the work of investigators mentioned below. Petrenko<sup>15</sup> studied twenty-five alloys covering the entire range

of compositions and presented a constitutional diagram for the system. The silver-rich end has been studied by Hoar and Rowntree<sup>1</sup> and Ageew and Shoyket.<sup>2</sup> The narrowness of the beta field has been confirmed by Westgren and Bradley.<sup>3</sup> Hansen<sup>4</sup> studied the aluminum-rich end of the system and confirmed the age-hardening properties noted by Kroll.<sup>5</sup>

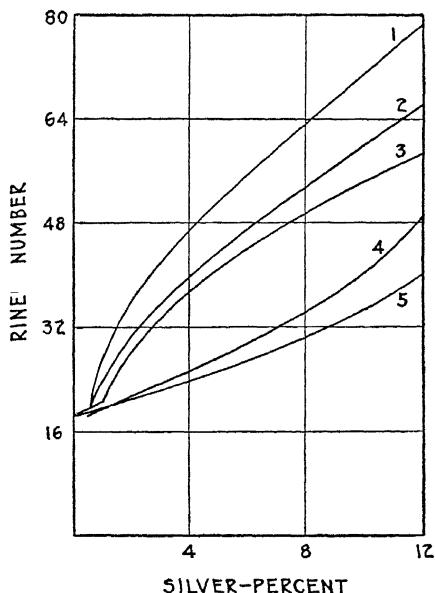
### (b) Properties

*Physical Properties.*—Hansen<sup>6</sup> studied the aging characteristics of samples of cast aluminum-silver containing from 0.45 to 11.8 per cent of silver quenched from 525 °C, Figure 3. At 100 °C the maximum hardness was not attained after 6-weeks' aging. Aging at 150 to 160° C gave the highest hardness. Quenching from 300 °C produced the softest state observed.

1. Aged for 5 days at 150 °C.
2. Aged to maximum hardness at 175 °C.
3. Aged for 32 days at 200 °C.
4. Heated for 5 hours at 525 °C and quenched.
5. Heated for 45 hours at 537 °C and quenched, and afterwards heated for 5 days at 300°±5° and quenched.

FIGURE 3.

The Brinell Numbers (5 mm, 62.5 kg, 30 sec) of aluminum-silver alloys of increasing silver content after various heat treatments (Hansen).<sup>6</sup>



Kroll<sup>5</sup> studied the age-hardening of aluminum containing 1.3 to 9.1 per cent of silver. He obtained about the same increase in hardness, as measured on the Brinell scale, as was observed on similar copper-aluminum alloys, but both the initial and final values were lower. The maximum tensile strength was about 11,400 lb/in<sup>2</sup> (8 kg/mm<sup>2</sup>) lower than the tensile strength of a copper-aluminum alloy containing 5 per cent of copper. The addition of 0.5 per cent of magnesium increased the maximum hardness obtainable in both cases, but the effect of mag-

nesium was to raise the aging temperature of the silver-aluminum alloys, whereas it lowered it for the aluminum-copper alloys.

Some work on aluminum-silver alloys has been done at the research laboratory of the Aluminum Company of America.<sup>7</sup> An aluminum alloy containing 5 per cent of copper and 3 per cent of silver and practically no  $Mg_2Si$  showed slightly better mechanical properties than the same alloy without silver, when aged at room temperature, but practically no improvement when aged at 143 °C. After salt-spray tests over a period of 4 weeks, the silver-containing alloy was found to have suffered a considerably greater decrease in ultimate tensile strength than the simple 5 per cent copper alloy. Microscopic examination revealed typical intergranular corrosion.

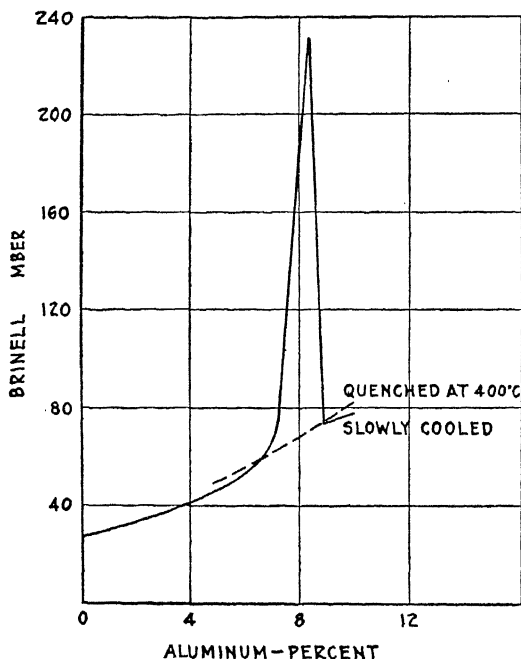


FIGURE 4.

Hardness of silver-aluminum alloys of increasing aluminum content after slow cooling and after quenching from 400 °C (Ageew and Shoyket<sup>8</sup>).

Other tests were made on an alloy of 30 per cent silver, and 70 per cent aluminum. As a solution treatment, the material was held at 540 °C for 2 hours, and quenched. After aging at 150 °C for 20 hours, the ultimate tensile strength was 48,000 lb/in.<sup>2</sup> the yield strength 46,000 lb/in.<sup>2</sup> and the elongation (2-inch gauge length) 2 per cent. When the same alloy was aged at room temperature after the same solution treatment, the corresponding values were 51,000 lb/in.<sup>2</sup> 37,000 lb/in.<sup>2</sup>

and 11 per cent. Material of this composition could be rolled readily either hot or cold. In cold-rolling, it was necessary to interrupt the process by an annealing after each reduction of 50 per cent. Although specimens of this alloy showed little disposition to tarnish, they corroded severely in moist air.

It is of interest to note that in the work done at the laboratories of the Aluminum Company of America, less silver could be gotten into solution than should have been possible according to Hansen's work on aluminum-rich alloys.

Addition of aluminum to silver was found by Jordan, Grenell, and Herschman<sup>8</sup> to increase the hardness rapidly with increasing aluminum content. Likewise Ageew and Shoyket,<sup>2</sup> working with cast alloys, found that, by cooling the alloy containing 7.9 per cent of aluminum rather slowly, a marked increase in hardness was obtained. Figure 4 shows the very narrow range over which this peculiar effect occurred.

Guillet and Guillet<sup>9</sup> studied aluminum-silver alloys containing 10.83 and 29.62 per cent silver. The Brinell number (10 kg/2 mm) of the 10.83 per cent alloy as cast was 35, and after heat treatment and aging 30 minutes at 150 °C the hardness was 51. Similarly, the hardness of the 29.62 per cent alloy increased from 44 to 90. A wrought specimen of the 10.83 per cent silver alloy did not age at room temperature, but showed a maximum aging effect after 45 minutes at 150 °C, the hardness increasing by 50 Brinell numbers from about 35 Brinell.

Data obtained by the Silver Project are summarized in Tables 2 and 3. Table 2 shows that the hardness of aluminum is increased by silver and *vice versa*. The response of these alloys to heat treatment was studied by B. S. Old. Only the 7, 10, and 92 per cent silver alloys showed noteworthy aging properties.

Table 2.—Hardness and Age-Hardening of Aluminum-Silver Alloys.

Silver (%)	Chill Cast Brinell*	Hardness— After Heat Treatment— Rockwell Number	
		Quenched	Aged
Trace	17	—	— <sup>1</sup>
0.12	17	—	— <sup>1</sup>
1.30	20	—	— <sup>1</sup>
7.00	42	5F	48F <sup>2</sup>
10.00	57	18F	63F <sup>2</sup>
71.00	91	96F	101F <sup>2</sup>
87.50	109	—	— <sup>1</sup>
89.50	104	—	— <sup>1</sup>
92.00	83	40B	97B <sup>3</sup>
94.90	45	—	— <sup>1</sup>
97.50	40	—	— <sup>1</sup>

<sup>1</sup> No aging detected.

<sup>2</sup> Wrought alloy, homogenized 24 hours at 500 °C, quenched, then aged 2 hours at 225 °C.

<sup>3</sup> Cast alloy, homogenized 24 hours at 700 °C, quenched, then aged 23½ hours at 245 °C.

\* 500-kg load, 10-mm ball.

Table 3.—Physical Properties of Aluminum-Silver Alloys.<sup>1,2</sup>

Silver (%)	Hardness Vickers No.		Tensile Strength p. s. i.		Yield Strength <sup>3</sup> p. s. i.		Elongation % in 2"		Resistivity Microhm-cn 20 °C.	
	An- nealed	C.R.	Annealed	C.R.	Annealed	C.R.	Annealed	C.R.	An- nealed	C.R.
Trace	18	33	8,920	13,300	2,900	12,100	33.5	7.5	2.9	2.9
0.12	18	34	8,500	10,600	3,200	10,300	31.0	2.0	3.0	3.1
1.30	20	41	10,100	13,300	4,100	11,100	31.0	4.0	3.2	3.4
7.00	49	56	25,600	32,100	11,600	28,900	20.0	4.0	3.7	3.8
10.00	73	87	31,200	38,700	15,600	34,300	23.0	8.0	4.4	4.4

<sup>1</sup> Annealed. At 500 °C for 1 hour.<sup>2</sup> Cold-rolled. 30% (No. 15 B. & S. to No. 18 B. & S. gauge).<sup>3</sup> 0.2% offset method.

The effect of 1.3, 7, and 10 per cent of silver on the annealing temperature of aluminum was noted. Sheet material which had been cold-rolled from No. 15 to No. 18 B. & S. gauge was used. The annealing temperature was not materially raised. The lower silver alloys maintained their cold-rolled hardness to 300 °C, but the 10 per cent alloy began to soften at 100 °C, passed through a minimum of about 55 Vickers at 300 °C, and rose to almost 100 Vickers on annealing at 400 °C, no doubt due to an aging effect.

The effect of 2.5 per cent of aluminum on the hardness and annealing properties of silver was determined. The annealing curve is shown in Figure 5. The general hardness was increased about 50 Vickers numbers and the annealing temperature raised about 100 °C. For material given a 30 per cent cold reduction to No. 18 B. & S. gauge, and annealing time of 1 hour, the full-annealing temperature is 350 °C.

*Electrical Properties.*—The electrical resistance of aluminum alloys containing small amounts of silver has been investigated by Fraenkel<sup>10</sup> and also by Böhner<sup>11</sup>, covering the range of 0.83 to 3.85 per cent silver. Their results are in good agreement with the Project data on the electrical resistance of similar alloys, as reported in Table 3.

According to Broniewski<sup>12</sup> alloys containing 0 to 60 per cent of silver possessed a higher resistance in the quenched than in the annealed state, the opposite being true with respect to the temperature coefficient of electrical resistance. He also reported a gradually increasing value of thermoelectric power of silver-aluminum alloys against lead with increasing silver content up to 60 per cent.

*Corrosion Resistance.*—DeMarchi<sup>13</sup> studied the corrosion of the aluminum alloys listed in Table 1. He found that the weight loss of the alloy, compared to that of high purity aluminum, is not increased by 0.12 per cent of silver, but is tripled by 1.3 per cent of silver, and is approximately 6-fold greater with 7 per cent of silver. This indicates the presence of a silver-rich phase producing galvanic corrosion. At the silver end of the system, up to 5.1 per cent of aluminum does not increase the corrosion of pure silver. With 8 per cent of aluminum in silver, a very high corrosion rate was observed. It may be concluded that while the silver-rich and the aluminum-rich solid solutions are

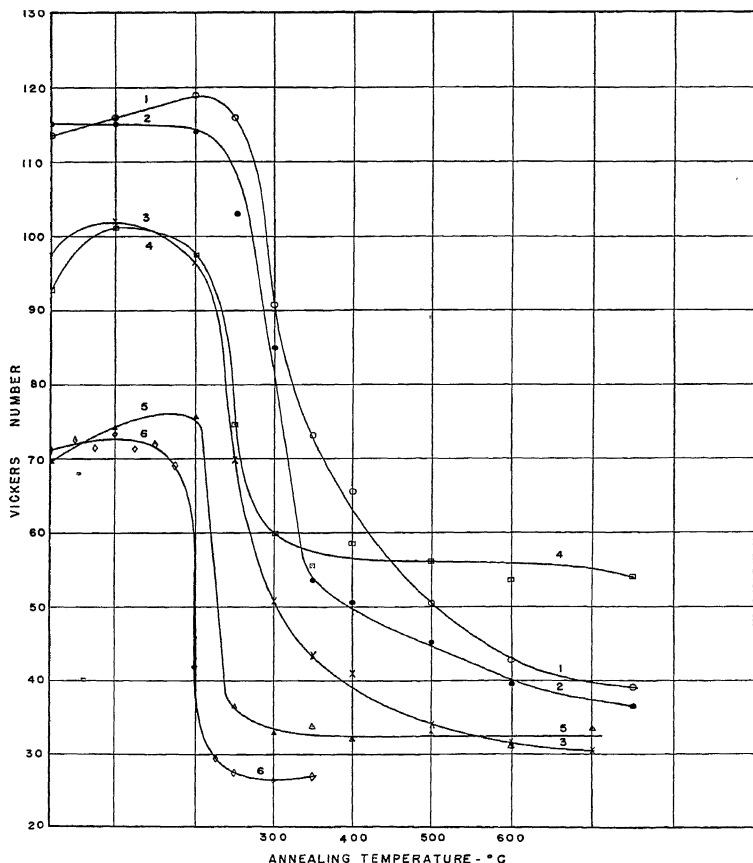


FIGURE 5. Effect of various elements on the annealing properties of silver.

- Curve 1. Antimony 5.8%, silver remainder.  
 2. Aluminum 2.5%, silver remainder.  
 3. Arsenic 2.3%, silver remainder.  
 4. Silicon 2.5%, silver remainder.  
 5. Manganese 2.5%, silver remainder.  
 6. Double-refined silver, 99.995%.

All specimens cold-rolled from No. 15 to No. 18 B. & S. gauge before annealing for 1 hour at indicated temperature.

each highly corrosion resistant, accelerated corrosion may be expected in alloys of aluminum and silver of duplex microstructure. However, in an indoor atmosphere, samples of aluminum alloys containing up to 10 per cent silver have remained bright for over a year.

*Reflectivity.*—The optical reflectivity of silver is reduced slightly by small amounts of aluminum. A reflection factor of 86 per cent was



obtained on the 2.5 per cent alloy; the 5.1 per cent alloy had a reflectivity of 81 per cent.

*Miscellaneous.*—The author has been advised <sup>14</sup> that alloys of aluminum with 2.5 to 4.0 per cent of silver can be worked cold and have a specific gravity of 3.0-3.5. As far as the informant was aware, no other cold-workable alloy with this specific gravity is known.

### (c) Applications

Little commercial use appears to be made of alloys largely comprised of aluminum and silver. The aluminum-rich alloys containing about 10 per cent silver, which are harder and whiter than aluminum, have been suggested for cheap jewelry because of their workability and pleasing color. A review of the patent literature \* suggests other possible uses. Solders for aluminum are mentioned (1,732,727 and 1,466,061); durable mirrors (1,982,774); a magnetic coinage alloy (1,590,091); a dental alloy (373,221), and more corrosion-resistant alloys (1,092,500 and 1,863,612).

For the most part, it appears that copper will improve aluminum much as silver does, but more cheaply. However, the improvement produced by adding small proportions of aluminum to silver appears to warrant further investigation.

## 2. Antimony-Silver

### (a) Constitution

Figure 6 is the diagram for antimony-silver alloys, as prepared by the Project, based on the work of Weibke and Efinger <sup>11</sup> and others. The constitution of antimony-silver alloys has been studied by Gautier,<sup>1</sup> Heycock-Neville,<sup>2</sup> Petrenko,<sup>3</sup> Raeder-Brun,<sup>4</sup> Westgren, Hägg and Eriksson,<sup>5</sup> Hansen and Sachs,<sup>6</sup> Pushin,<sup>7</sup> Guertler and Rosenthal,<sup>8</sup> Broderick and Ehret,<sup>9</sup> Reynolds and Hume-Rothery,<sup>10</sup> and by Weibke and Efinger.<sup>11</sup>

According to Broderick and Ehret,<sup>9</sup> the solubility of antimony in silver is 6 per cent, and with more than 28 per cent antimony,  $\epsilon'$  is in equilibrium with almost pure antimony. On the other hand, Hansen and Sachs<sup>6</sup> found an indication of a solubility of about 5 per cent silver in antimony, based on electrical resistivity measurements. Weibke and Efinger<sup>11</sup> explored alloys containing from 17 to 31 per cent antimony by thermal, microscopic, and x-ray methods, and presented a diagram showing the constitution of the system in the region 0 to 35 per cent antimony.

Reynolds and Hume-Rothery<sup>10</sup> determined the liquidus curve accurately in the range 0-25 atomic per cent antimony. The peritectic horizontal was located at 702.5 °C, and the epsilon phase was found to have a close-packed hexagonal structure. The phase boundaries of

\* See Appendix II, Section 2. All patents cited here are United States patents.

the two solid solution phases at the silver end of the diagram were determined accurately above 300 °C. The solid solubility of antimony in silver is given as 8.05 per cent at the peritectic temperature, and as 6.2 per cent at 300 °C. The  $\epsilon'$  phase is the  $\text{Ag}_3\text{Sb}$  phase.

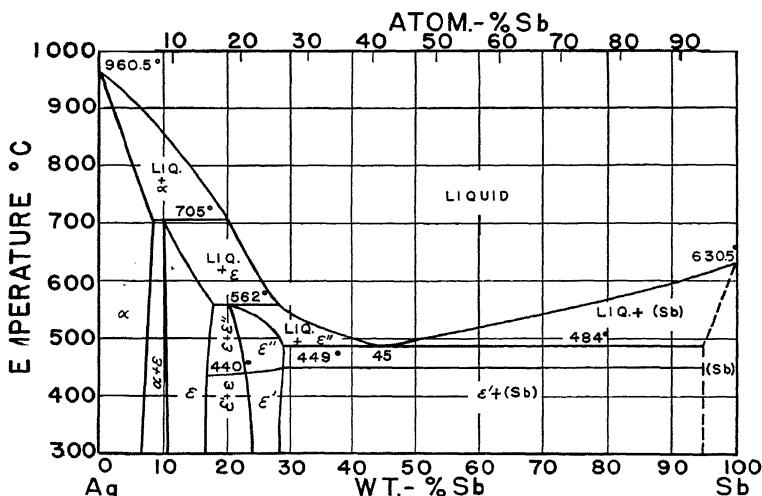


FIGURE 6. Antimony-silver constitutional diagram.

Weibke and Efinger: *Z. Elektrochem.*, 46, 61 (1940), et al.

### (b) Properties

Some physical properties of silver containing 5.8 per cent of antimony are shown in Table 4, as determined by the Silver Project staff.

Table 4.—Physical Properties of Silver-5.8 Per Cent Antimony Alloy.

Condition of Material	Vickers Number	Tensile Strength p. s. i.	Yield Strength <sup>3</sup> p. s. i.	Elongation % in 2"	Resistivity Microhm-cm. 20 °C.
As-rolled <sup>1</sup>	113	51,600	50,600		41
Annealed <sup>2</sup>	45	34,400	5,800	69	38

<sup>1</sup> Cold-rolled from No. 15 to No. 18 B. & S. gauge.

<sup>2</sup> One hour at 700 °C.

<sup>3</sup> 0.2% offset method.

The effect of annealing cold-worked material of this composition is shown in Figure 5. An alloy containing 6.76 per cent antimony was hot-rolled successfully, and cold-rolled from 0.150 to 0.110 inch thickness before the sample cracked. The samples of higher antimony content could not be worked, either hot or cold. Jordan, Grenell and

Herschman found that the strength of the 5 per cent alloy was greater than that of the corresponding tin alloy, but less than that for the 5 per cent aluminum composition. Their efforts to roll the 10 per cent alloy were unsuccessful. Its color was gray and the 15 per cent alloy was a still darker gray. They also reported that antimony reduced the tarnish formation on silver. From the constitutional diagram it may be anticipated that alloys consisting only of the silver-rich solid solution would be workable, while those alloys containing the harder intermediate phase or phases would be relatively brittle.

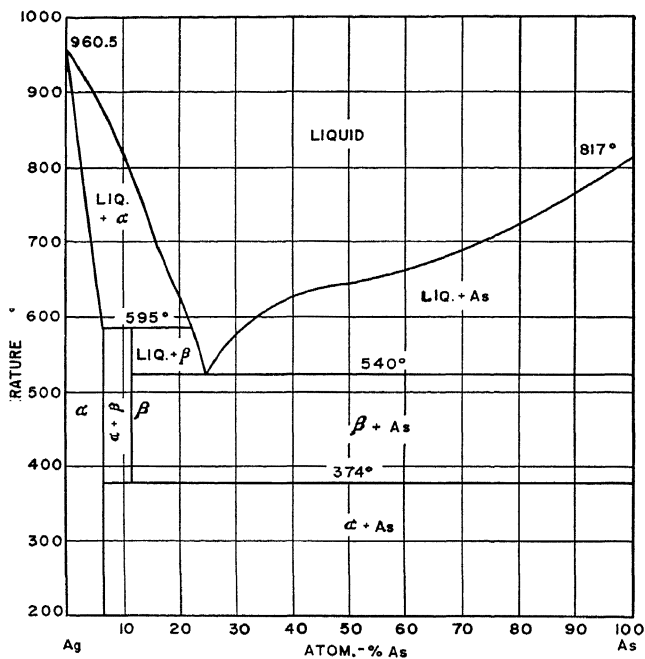


FIGURE 7. Arsenic-silver constitutional diagram.

Heike & Leroux: *Z. anorg. Chem.*, 92, 119 (1915).

### (c) Applications

No use seems to have been made of the binary silver-antimony alloys, although the physical properties, workability and color of the 5.8 per cent antimony alloy are interesting. The corrosion resistance of this alloy exposed to hydrochloric acid and chlorides should be investigated as it is possible that the formation of antimony oxy-chloride will increase the stability of the protective chloride film which tends to form on silver.

United States Patent 2,032,912 advocates the production of a hard layer of white  $\text{Ag}_3\text{Sb}$  on silver by plating the silver with antimony and then heating the plated object just enough to produce a diffusion layer at the surface of this composition. United States Patent 1,628,673 claims a tarnish-resistant alloy of sterling composition and quality containing antimony and cadmium, while patents number 1,970,319 and 2,052,142 claim tarnish-resistant silver alloys of sterling fineness containing tin and antimony.

According to U. S. Patent 2,053,662 powdered  $\text{Ag}_3\text{Sb}$  can be used to raise the annealing temperature of copper commutator segments produced by compressing and sintering the mixed powders.

### 3. Arsenic-Silver

#### (a) Constitution

Figure 7 is the constitution of the silver-arsenic system as reported by Heike and Leroux,<sup>1</sup> who used thermal and microscopic methods to supplement the work of Friedrich and Leroux.<sup>2</sup> Broderick and Ehret<sup>3</sup> made an x-ray crystal structure examination of the system which, in general, supports the thermal diagram of Heike and Leroux.

#### (b) Properties

Table 5 presents data obtained by the Project on the properties of an alloy containing 2.28 per cent arsenic. The alloy was workable, white in color, and has annealing properties shown in Figure 5. Although

Table 5.—Physical Properties of Silver-2.28 Per Cent Arsenic Alloy.

Condition of Material	Vickers Number	Tensile Strength p. s. i.	Yield Strength <sup>3</sup> p. s. i.	Elongation % in 2"	Resistivity Microhm-cm. 20 °C
As-rolled <sup>1</sup>	97	44,000	40,400	15	25
Annealed <sup>2</sup>	32	28,100	4,400	71	21

<sup>1</sup> Cold-rolled from No. 15 to No. 18 B. & S. gauge.

<sup>2</sup> One hour at 700 °C.

<sup>3</sup> 0.2% offset method.

this alloy tarnishes less readily than pure silver, it is by no means tarnish-resistant.

#### (c) Applications

No applications are known.

### 4. Barium-Silver

#### (a) Constitution

Figure 8 is the barium-silver constitutional diagram according to Weibke.<sup>1</sup>

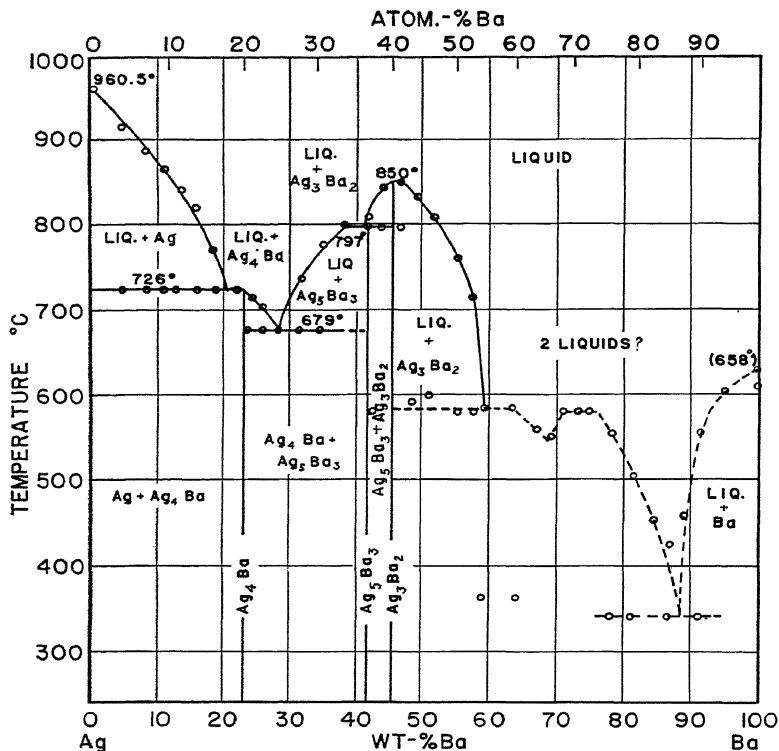


FIGURE 8. Barium-silver constitutional diagram.

Weibke: *Z. anorg. Chem.*, 193, 297 (1930).**(b) Properties**

Ray and Baker<sup>2</sup> report that barium-silver alloys which they made were hard, nonmalleable, and easily tarnished when the barium was present to the extent of 10 per cent or more.

R. W. Dayton<sup>3</sup> reported that silver to which barium had been added (nominal analysis 2½ per cent) exhibited good antifriction properties, but this result may have been a consequence of the deoxidizing effect of barium rather than of any true alloying effect.

**(c) Applications**

According to U. S. Patent 1,925,978, a nickel-barium silver alloy has useful electron-emission properties. No other applications are known, although barium might be useful as a deoxidizer for silver-rich melts.

## 5. Beryllium-Silver

## (a) Constitution

Figure 9 is the constitutional diagram for beryllium-silver alloys according to Winkler.<sup>1</sup> Winkler used x-ray, metallographic, thermal, and magnetic methods to revise the diagram as presented by Sloman<sup>2</sup> based on the work of Oesterheld,<sup>3</sup> Jaeger<sup>4</sup> and Sloman.<sup>5</sup> Winkler<sup>1</sup> confirmed the existence of two intermetallic phases at 63 and 73 atomic per cent of beryllium which decompose on cooling, and that the solid solubility of silver in beryllium is not more than 3 atomic per cent.

## (b) Properties

Cooper, in British Patent 399,261, claims that silver alloys containing more than 90 per cent silver and 3 to 5 per cent beryllium are immune to the action of sulfur and its compounds and that such alloys, while brittle in the chill-cast state, can be rendered almost as ductile as silver itself by suitable heat-treatment. Sloman<sup>2</sup> confirmed Cooper's claims, but found the alloys unsatisfactory owing to their relatively high beryllium content, and himself patented alloys of this type containing up to 1 per cent of beryllium. Sloman contends that the maximum immunity to tarnish was obtained with about 0.4 per cent of beryllium and that larger proportions, which are in excess of the solid solution limit, lead to the objectionable presence of particles of a harder phase. Although some workers, including Jordan, Grenell and Hersch-

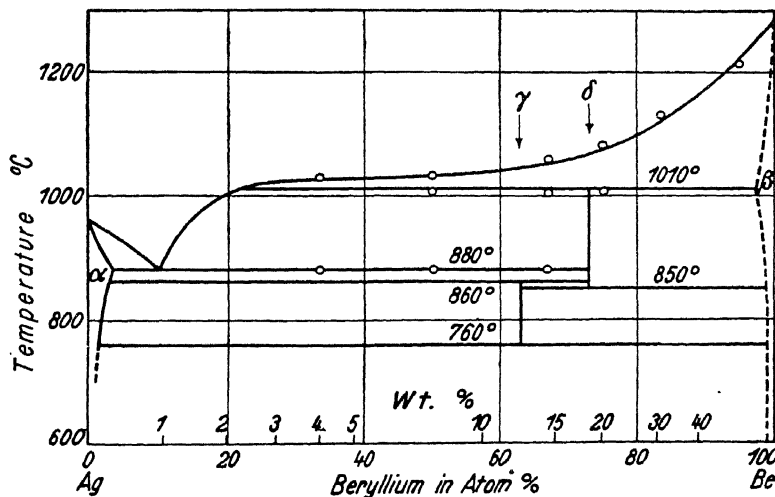


FIGURE 9. Beryllium-silver constitutional diagram.

Winkler: *Z. Metallkunde*, 30, 162 (1938).

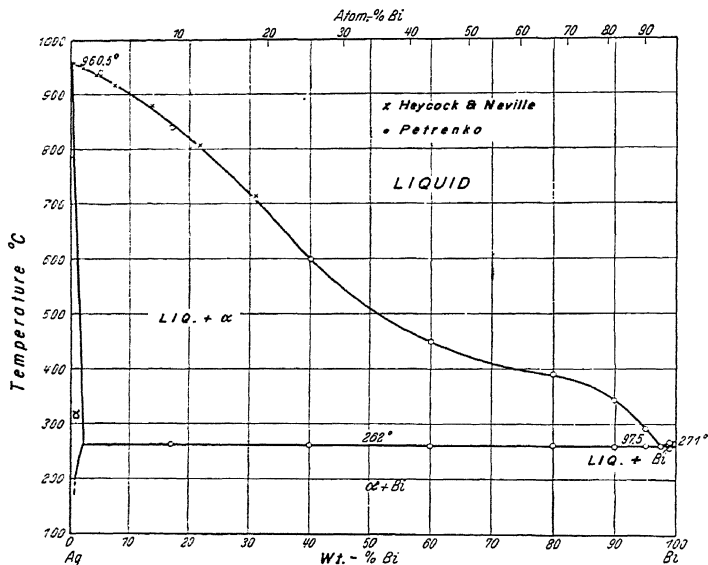


FIGURE 10. Bismuth-silver constitutional diagram.

Chiswick and Hultgren: *Metals Tech.*, TP 1169, April, 1940.Petrenko: *Z. anorg. allgem. Chemie*, 50, 136 (1906).Heycock and Neville: *Phil. Trans. Roy. Soc. (A)*, 189, 67 (1897).

man, did not find the improvement in tarnish resistance which Sloman claimed, Price and Thomas<sup>6</sup> have shown that it is possible to produce a transparent protective film of beryllium oxide on high-silver alloys, containing a small percentage of beryllium, by selective oxidation. This film is quite protective against tarnish, although readily abraded. The tarnish-resistance of silver containing beryllium will probably vary with the condition of the surface film.

### (c) Applications

Interest in alloys of this class has been in a material of sterling fineness but of improved resistance to tarnish (Brit. Pat. 399,261; U. S. Pat. 1,984,225 and 2,031,113). An application of silver-beryllium alloys which is being exploited commercially is in copper-base alloys to which silver and beryllium impart hardening ability but do not greatly reduce the electrical conductivity. The alloy may contain tin, manganese, magnesium or cobalt, as well as minor additions of silver and beryllium (U. S. Pat. 2,094,789; 2,126,386; 2,126,633; 2,131,104; 2,136,919 and 2,143,914). Somewhat similar alloys containing a substantial proportion of silver have also been patented (U. S. Pat. 2,046,056; 1,928,429; 2,020,949).

## 6. Bismuth-Silver

## (a) Constitution

Figure 10 is the constitutional diagram for bismuth-silver alloys according to the combined data of Heycock and Neville,<sup>1</sup> Petrenko,<sup>2</sup> and Chiswick and Hultgren.<sup>3</sup> The latter investigators report that the solubility of silver in bismuth is too low to be detectable. The solubility of bismuth in silver is 1.5 per cent at 260 °C, and 0.6 per cent at 200 °C, far less than that reported by Broderick and Ehret.<sup>4</sup>

## (b) Properties

Reference to the literature indicates some interesting electrical and magnetic properties of silver-bismuth alloys.

## (c) Applications

No applications of importance are known.

## 7. Cadmium-Silver

## (a) Constitution

Figure 11 is the constitutional diagram for cadmium-silver alloys according to Owen, Rogers and Guthrie.<sup>1</sup> Durrant<sup>2</sup> studied the cad-

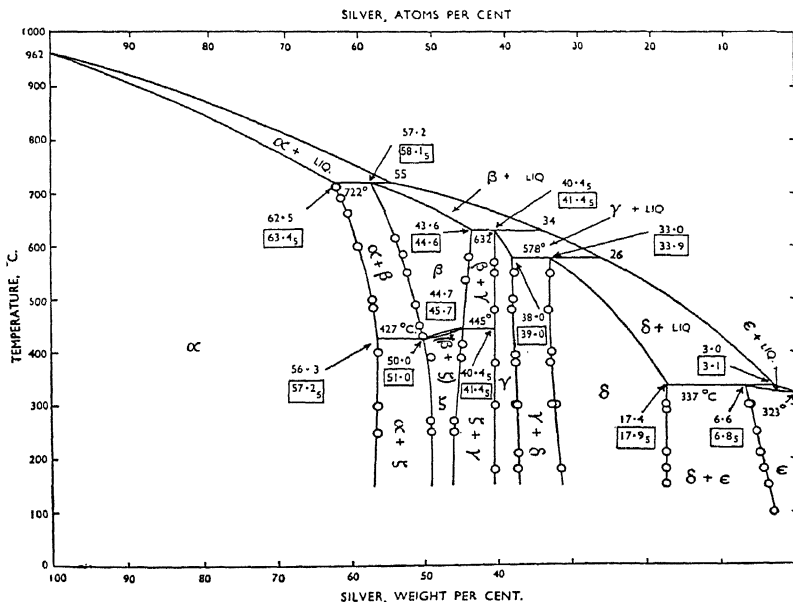


FIGURE 11. Cadmium-silver constitutional diagram.

Owen, Rogers, and Guthrie: *J. Inst. Metals*, 65, 231 (1939).



mium-rich alloys containing up to 40 per cent of silver. Nearly 43 per cent of cadmium is soluble in silver at room temperature. The intermediate alloys have been studied by x-ray methods by Astrand and Westgren<sup>3</sup> and by Natta and Freri,<sup>4</sup> while Fraenkel and Wolf<sup>5</sup> have used thermal and dilatometric, electrical resistance and other methods. Ölander<sup>6</sup> measured the electromotive force and the temperature coefficient of electromotive force of a number of alloys against molten cadmium. Perakes and Capatos<sup>7</sup> made a thermomagnetic study of the silver-cadmium system.

### (b) Properties

Alloys containing 50 per cent by weight of cadmium are brightly colored, a fact that was first commented upon by Heycock and Neville.<sup>8</sup> Rose<sup>9</sup> noted colors ranging from red to lilac and stated that these appeared upon quenching alloys containing 43 to 50 per cent of silver from above a transformation point occurring in the vicinity of 420 °C. He attributed the effect to surface oxidation. Schreiner<sup>10</sup> noted a series of colors as the composition was changed. His alloys appear to have cooled rather slowly through the transformation, somewhat above 400 °C, but since they were removed from the furnace at a temperature estimated to be above 200 °C, they may have dropped rather quickly through the thermal critical point, which occurs in this neighborhood.<sup>6</sup> Schreiner also observed that alloys containing 40 to 50 per cent silver showed a marked change in their electromotive force against cadmium after standing for several months at room temperature.

Information on the mechanical properties of the cadmium-silver alloys is scanty. Those of intermediate composition are generally brittle. Schreiner<sup>10</sup> reported that an alloy containing 40 per cent silver broke while being shaken in a flask. Fraenkel and Wolf<sup>5</sup> noted the extraordinary brittleness of alloys containing 37.3 and 42.0 per cent silver and stated that material containing 44.1 per cent silver could be readily broken with a hammer. It appears from their work, however, that alloys containing 46 to 59 per cent silver may be worked by the ordinary process of drawing and rolling. According to Owen, Rogers and Guthrie,<sup>1</sup> the gamma-phase alloys were very brittle, and alloys in the beta phase, when quenched from temperatures above 600 °C, were plastic.

Rose<sup>9</sup> considered a specimen containing 65 per cent silver to be

Table 6.—Change of Hardness of Cadmium-Silver Alloy (49 per cent of Silver) with Heat Treatment.<sup>11</sup>

Treatment	Brinell number (5 mm, 500 kg, 15 sec)
As cast	100
Annealed at 500 °C	119
Quenched from 400 °C	77
Reheated at 150 °C	115
Reheated at 320 °C	84

less ductile than those which contained more silver. Fraenkel and Wolf measured the hardness of the intermediate alloys, 40 to 60 per cent silver, by the Brinell method and obtained values from 60 to 70 on alloys which had been annealed for a long time at 180 °C. They also found that quenching from 300 and 500° C produced only small changes in hardness. According to Guillet and Cournot<sup>11</sup> alloys containing approximately 60.0 per cent silver exhibited only slight change with heat treatment, the hardness (Brinell scale) being about 35 to 45. Alloys containing 49.3 per cent silver, however, showed appreciable changes with heat treatment, as shown in Table 6.

The alloy containing 95 per cent cadmium and 5 per cent silver has been investigated in more detail. The data given in Table 7 have been supplied by Handy & Harman.

Table 7.—Tensile Properties of the 95 per cent Cadmium-5 per cent Silver Alloy at Various Temperatures.

Temperature at Test (°F)	Ultimate Tensile Strength (lb/in <sup>2</sup> )	Elongation in 2" (%)	Reduction of Area (%)
Room temperature	16,400	31.3	81.0
300	4,400	93.7	91.0
425	2,600	93.7	68.0
500	1,700	21.9	11.0

The values were obtained on  $\frac{1}{4}$ -inch rods at ordinary rate of load application and the values should be considered as only approximate. The load required to produce continuous stretch at room temperature was found to be about 1,200 lb/in.<sup>2</sup>

The 95 per cent cadmium-5 per cent silver alloy melts at 640 °F (338 °C) and flows freely at 740 °F (393 °C). It has good soldering properties and its use as a solder is discussed in Chapter 7.

Jordan, Grenell and Herschman<sup>12</sup> were able to roll alloys containing from 5 to 25 per cent cadmium. They found that the 5 per cent cadmium alloy exhibited no greater tensile strength or hardness than pure silver. The alloy containing 25 per cent cadmium did not approach sterling silver or the 5 per cent aluminum alloy in strength or hardness. They noted an unmistakable yellow color in the alloys containing 20 and 25 per cent cadmium, and that cadmium was effective in reducing sulfide tarnish formation.

Some interest has been shown in the chemical properties of silver-cadmium alloys, principally those containing considerable silver. It was noticed by Rose<sup>9</sup> that silver-cadmium alloys did not tarnish as readily when immersed in a solution of ammonium polysulfide as did copper-silver alloys of corresponding composition. He also observed that the brittle alloys of the intermediate range of composition were resistant to cold nitric acid, hydrochloric acid, and some reagents. The simultaneous electrodeposition of silver and cadmium has been studied

by a number of investigators.<sup>13-19</sup> Stillwell and Stout<sup>14</sup> showed by x-ray methods that the deposits consisted of definite phases of the cadmium-silver system rather than a mixture of the two metals. They also observed that, for a given composition, the phases were not generally present in the same proportions as in the corresponding alloy made by melting in the ordinary way.

### (c) Applications

The principal industrial applications of the cadmium-silver alloys are the solder described in Table 7 and a cadmium-copper-silver bearing metal. The principal advantage of the cadmium-silver solder over the lead-tin solders is its considerably higher strength at both room and elevated temperatures.

The cadmium-copper-silver bearing alloy contains approximately 97 per cent cadmium, 0.5 per cent copper, and 2 per cent silver. According to the manufacturer,<sup>20</sup> this bearing has the properties described in Table 8.

Table 8.—Tensile Strength of the Cadmium-Copper-Silver Bearing Metal at Various Temperatures<sup>20</sup>

Temperature At Test (°F)	Ultimate Tensile Strength (lb/in <sup>2</sup> )	Elongation in 2" (%)	Brinell Hardness Number (As cast)
Room temperature	18,000	50	40.2
212	12,000	—	19.0
300	8,000	—	13.2
400	4,350	68	8.1

Other uses of interest are in high-silver alloys for brazing, electrical contacts, tarnish-resistant alloys, and as minor additions to copper. The patent literature contains many references to such application; only a few typical ones will be mentioned. According to the claims of U. S. Patents 1,215,138; 1,899,701 and 1,899,873, alloys containing not less than 48 per cent silver and a substantial proportion of cadmium are useful for low-temperature brazing purposes. Some of these alloys may contain copper, zinc, tin, nickel and phosphorus. Alloys containing about 80 per cent of silver and the remainder largely cadmium are suitable for electrical contacts according to U. S. Patents 1,940,962; 2,058,857 and 2,099,551; these alloys may also contain some platinum, palladium, lead, manganese, nickel, copper, and cobalt. U. S. Patents 1,628,673 and 1,896,410 are representative of a group claiming an alloy of approximately sterling fineness and quality, but of improved resistance to tarnish; such alloys may contain small amounts of copper, antimony, tin and nickel. Patents covering the use of small additions of cadmium and silver to copper, in order that a high-strength, high-conductivity alloy will result, include U. S. Patents 1,891,495 and 2,049,500.

## 8. Calcium-Silver

## (a) Constitution

Figure 12 is the constitutional diagram for calcium-silver alloys based on the work of Baar,<sup>1</sup> who made a thermal and microscopic investigation of these alloys.

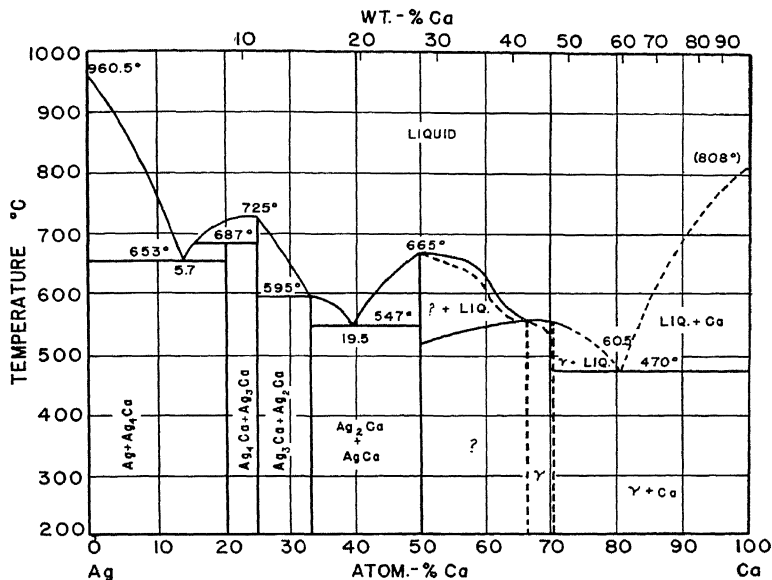


FIGURE 12. Calcium-silver constitutional diagram.

Baar: Z. anorg. allgem. Chem., 70, 383 (1911).

## (b) Properties

Baar<sup>1</sup> states that the alloys containing 0-25 per cent calcium did not decompose water, those containing 25 to 35 per cent calcium had a weak action, and the higher calcium alloys readily decomposed water with the evolution of hydrogen. The addition of calcium to silver increased the hardness but little and produced brittle alloys. Tammann and Rührenbeck<sup>2</sup> claim that alloys containing from 12 to 16 per cent of calcium attack water but slightly, whereas all alloys containing more than 16 per cent of calcium decompose water with vigor.

## (c) Applications

No applications are known, although U. S. Patent 1,970,318 covers the addition of less than 1 per cent of calcium to silver alloys containing 85 per cent or more of silver and a small percentage of tin.

## 9. Carbon-Silver

### (a) Constitution

According to Ruff and Bergdahl,<sup>1</sup> molten silver can dissolve 0.0012 per cent of carbon at 1660 °C and 0.0025 per cent at 1735 °C. Hempel<sup>2</sup> also found about the same solubility of carbon in molten silver. On cooling the silver, the carbon crystallizes out as graphite.

### (b) Properties

Silver forms, through chemical reaction, a compound containing 10.01 per cent of carbon. This is the acetylide  $\text{Ag}_2\text{C}_2$ , which has no metallic properties and is explosively unstable.

### (c) Applications

The use of carbon-silver electrical contacts for railway switch signals is important. Some use is also made of brushes composed of carbon and silver for sliding contacts. This application has been considered by Wiltse, Miles, and Parshall<sup>3</sup> in Chapter 13. For such applications the alloy is prepared by powder metallurgy methods. The electrical characteristics and performance will depend on the method of preparation, relative proportion of the constituents, and form of carbon employed.

Porous carbon has been considered as a support for finely divided, oligodynamically active silver.<sup>4</sup>

Wear tests carried out by Lane<sup>5</sup> on silver-graphite specimens running without any lubricant, against a rotating cast-iron drum and against a case-hardened drum showed far lower wear for silver-graphite (11.3 per cent by weight of graphite) than for pure silver. For both types of material, specimen wear was substantially less on the hardened drum than on the gray cast-iron drum (Brinell 230). Wear of the cast-iron drum was negligible in both instances, and also of the hardened drum operated against the silver-graphite specimen; however, the hardened drum showed appreciable wear after operating against pure silver. In another series of tests, specimens were used containing from 3 to 12 per cent by weight of graphite and operated dry against the cast-iron drum. Although the specimen and drum wear values did not vary greatly with the per cent of graphite, the 3 and 5 per cent alloys wore smoothly with very little "lipping;" the higher graphite samples "lipped" badly, indicating inferior load-carrying qualities. The 5 per cent alloy appears to have performed best.

## 10. Cesium-Silver

### (a) Constitution

The author has found no references pertaining to the constitution of the cesium-silver system.

## (b) Properties

A mosaic of minute silver particles on a mica sheet in a vacuum tube can be made photo-sensitive by admitting cesium vapor to the tube and by passing a glow discharge through the tube in an atmosphere of oxygen.<sup>1</sup>

## (c) Applications

The commercial application of cesium-silver alloys appears limited to use in photoelectric cells. This application has been discussed in Chapter 2, and additional references will be found in section H2 of Appendix I and section 7b of Appendix II.

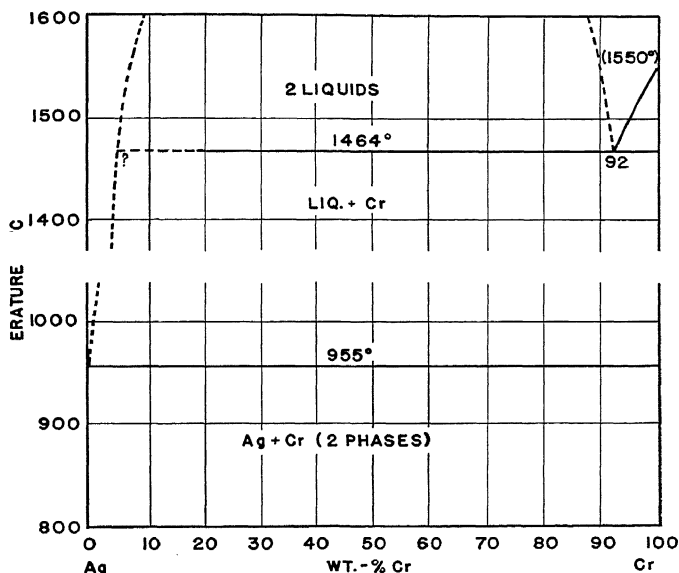


FIGURE 13. Chromium-silver constitutional diagram.

Hindrichs: *Z. anorg. allgem. Chem.*, 50, 423 (1908).

## 11. Chromium-Silver

## (a) Constitution.

Figure 13 is the constitutional diagram for chromium-silver, based on the work of Hindrichs,<sup>1</sup> which, however, is none too satisfactory as his melts were contaminated by iron, silicon, and nitrogen. Neither Bradley and Ollard<sup>2</sup> nor Sillers<sup>3</sup> conclusively settled the question of polymorphism in chromium, and this system may be revised in the light of investigations yet to be made. Hindrichs<sup>1</sup> indicates that liquid

chromium may dissolve up to ten per cent of silver, although the solidified mixture is composed only of the pure metals.

### (b) Properties

Jordan, Grenell and Herschman<sup>4</sup> were able to roll sheets of silver-chromium alloys analyzing 0.14 and 0.77 per cent chromium. The higher chromium alloy had the following properties in the annealed condition: tensile strength 28,500 pounds per square inch, elongation of 41 per cent in 0.5 inch, and Brinell hardness of 53 as measured on the "Baby Brinell" (12.8-kg load, 1.6-mm ball). Dehlinger<sup>5</sup> has investigated the crystal structure and magnetic properties of chromium-silver alloys.

### (c) Applications

Some use is being made of a copper alloy containing small chromium and silver additions, according to Brace.<sup>6, 7</sup> The applications are typical of those for a hardened, high-conductivity alloy. The use of silver in stainless steels is discussed under iron-silver alloys in this chapter.

The patent literature mentions the use of small percentages of silver and chromium in high-conductivity copper alloys, which may also contain small proportions of beryllium or cadmium (U. S. Patents 2,045,138, 2,046,056 and 2,049,500). According to U. S. Patent 1,952,082, a silver-tin alloy of sterling fineness has somewhat improved physical properties and tarnish resistance imparted by a fractional percentage of chromium. Tarnish-resisting silver-chromium deposits may be produced on silver by electrolytic means, according to claims made in U. S. Patent 1,782,092.

## 12. Cobalt-Silver

### (a) Constitution

According to Petrenko<sup>1</sup> silver and cobalt are practically insoluble in each other at 1600 °C. The solidified alloy consists of a mixture of the two pure metals. Tammann and Oelsen<sup>2</sup> report that 0.0004 to 0.0007 per cent cobalt is soluble in silver.

### (b) Properties

The effect of silver on the allotropic transformation of cobalt is discussed by Hashimoto.<sup>3</sup> Ducelliez<sup>4</sup> states that the alloys are comprised of a mixture of the two pure phases, and their magnetism is in proportion to the cobalt content. The electromotive force of the alloys in a normal solution of cobalt sulfate corresponds to that of cobalt metal. Mathers and Johnson<sup>5</sup> were able to co-deposit cobalt with silver from thiourea and thiocyanate baths. The presence of cobalt in a silver deposit noticeably increased the hardness but not the tarnish resistance of silver. Price, Smithells and Williams<sup>6</sup> studied a sintered alloy consisting of 4 per cent silver, 6 per cent cobalt, and 90 per cent tungsten.

Its density was  $10.7 \text{ g/cm}^3$  compared with a "theoretical" value of  $17.5 \text{ g/cm}^3$ .

### (c) Applications

The patent literature indicates some use for small amounts of silver and cobalt in (a) noble-metal alloys, (b) high-conductivity, copper-base alloys containing a fractional percentage of beryllium, as well as in some high-silver electrical contact alloys of complex nature.

## 13. Copper-Silver

### (a) Constitution

Figure 14 is the constitutional diagram for copper-silver alloys, as given by Smith.<sup>9</sup> Because of their importance in sterling ware and in coinage, the copper-silver alloys have been studied more thoroughly than any other of the alloys of silver with the common metals. The

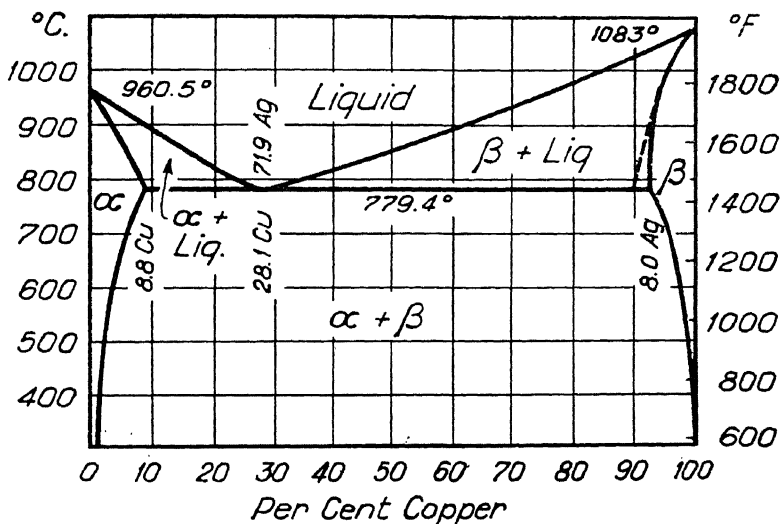


FIGURE 14. Copper-silver constitutional diagram.

Smith: A. S. M. Handbook, p. 1360, (

studies of Heycock and Neville,<sup>1</sup> Friedrich and Leroux,<sup>2</sup> Roeser,<sup>3</sup> Stockdale,<sup>4</sup> Smith and Lindlief,<sup>5</sup> Ageew and Sachs,<sup>6</sup> Hansen, Ageew, and Sachs<sup>7</sup> and others, on the constitutional diagram have been critically reviewed by Gregg.<sup>8</sup> Smith<sup>9</sup> has also critically reviewed data on the constitution of the copper-silver alloys.



## (b) Properties

1. *Physical*.—This diagram suggests that age-hardening should occur in copper alloys containing several per cent of silver. Smith and Lindlie<sup>5</sup> found such an effect, but it was small in comparison with that observed in the high-silver alloys. The maximum increase in hardness, B68 to B78, Rockwell scale, which was observed, was on an alloy containing 5 per cent silver which had been heated for 4 hours at 400 °C. The observed changes in tensile strength, elongation, and electrical conductivity of this alloy are shown in Figure 15.

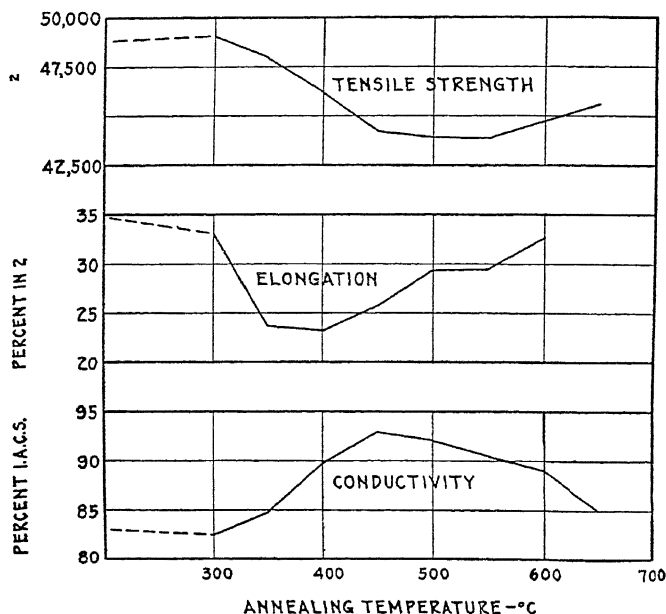


FIGURE 15. Effect of annealing on properties of a copper-silver alloy after being quenched from 750 °C.<sup>5</sup>

The hardness of annealed cast specimens was found by Kurnakow, Puschin, and Senkowsky<sup>10</sup> to increase from about 40 to 60 on the Brinell scale (10-mm ball, 100-kg load) as the silver content was increased from 0 to approximately 5 per cent. On wrought material, Norbury<sup>11</sup> observed a somewhat smaller rise in hardness over the same range.

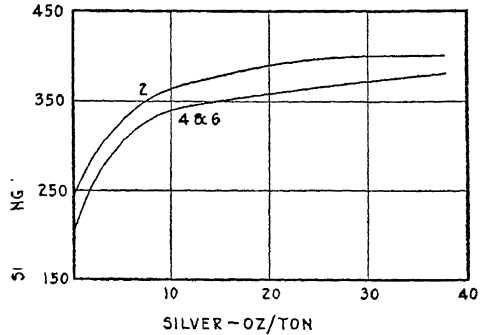
Perhaps the most interesting result of adding small amounts of silver to copper is the increase in "annealing temperature," as illustrated in Figure 16 from Kenny and Craig.<sup>12</sup> Annealing periods of  $\frac{1}{2}$  hour were

FIGURE 16.

Influence of silver on the softening temperature on annealing of hard copper sheet.<sup>12</sup>

Upper curve, sheet reduced 20 per cent; 2 numbers hard.

Lower curve, sheets reduced 37 and 50 per cent; 4 and 6 numbers hard, respectively (oz/ton  $\times 0.00343$  = per cent Ag).



employed and the hardness was measured by a Rockwell hardness tester.

The effect of annealing at 200 °C for long periods upon the ultimate tensile strength of argentiferous copper wires drawn from  $\frac{1}{16}$ -inch hot-rolled rods to 0.050-inch wire without annealing is shown in Figure 17. It will be observed that the silver content exerts a considerable effect. For an annealing temperature of 150 °C the decrease in tensile strength of the alloys very low in silver was much less marked. The strength of alloys containing above 0.03 per cent silver fell off slightly in the beginning, but showed practically no change in the interval from 150 to 365 days. Annealing for periods of 2 minutes was found by Kenny and Craig<sup>12</sup> to have marked effect on the tensile strength of hard-drawn

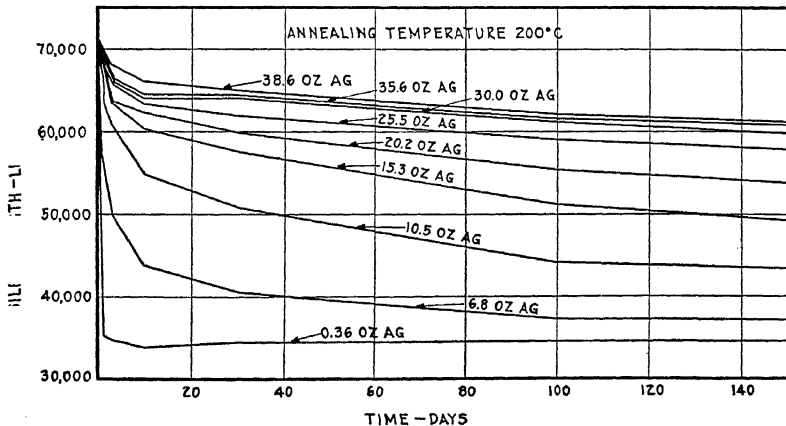


FIGURE 17. Tensile strength of 16-gauge (0.050 in.) wire after heating at 200 °C.<sup>12</sup>  
Silver content expressed as oz/ton. (Oz/ton  $\times 0.00343$  = per cent Ag.)

argentiferous copper wire, Figure 18. The amount of silver has an important influence on the amount of softening which takes place.

Among earlier investigators who studied the effect of small amounts of silver on copper may be mentioned Caesar and Gerner,<sup>13</sup> Johnson,<sup>14</sup> Hudson and McKeown,<sup>15</sup> Tapsell and Johnson<sup>16</sup> and Hudson, Herbert, Ball, and Buckell.<sup>17</sup> The last investigators found that additions of

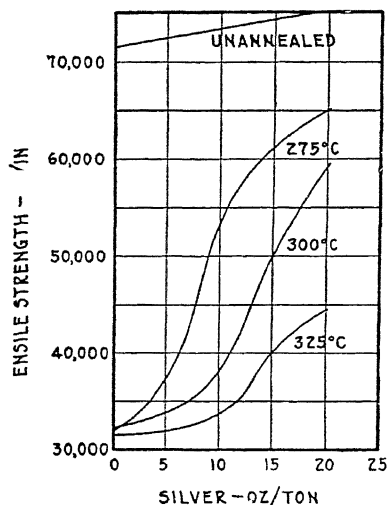


FIGURE 18.

Tensile strength of 24-gauge (0.020 in.) wire after annealing for 2 minutes at several temperatures.<sup>12</sup>

(Oz./ton  $\times 0.00343$  = per cent Ag.)

silver, iron, tin, and other elements were effective in raising the limit of proportionality of copper which had been cold-worked and then annealed at 300 °C. In their opinion silver was the most effective. They also stated, "The highest limits of proportionality observed in all alloys except copper containing silver were only obtained at the expense of ductility or with a hardness greater than that desired, or both."

Table 9.—Limit of Proportionality and Ultimate Tensile Strength of Plain Copper and Some Alloyed Copper, Annealed for 2 Hours at 300 °C.<sup>15</sup>

Material	Limit of proportionality (lb/in <sup>2</sup> )	Ultimate tensile strength (lb/in <sup>2</sup> )	Elongation [gauge length 4√area] (%)
High-conductivity copper	5,100	32,500	52
Arsenical copper	10,300	33,200	46.5
Silver-copper	7,200	34,300	51.0
Silver-arsenical copper	11,200	35,200	51.0

Hudson and McKeown<sup>15</sup> investigated the effect of variable amounts of silver in copper-silver and copper-silver-arsenic material for locomotive fire-box stays and plates. The silver content was of the order

of 0.1 per cent and the arsenic about 0.33 per cent. In tests at room temperature, the addition of silver was found to improve the tensile properties of both plain copper and the copper-arsenic alloy, particularly after annealing at about 300 °C. The results in Table 9 are representative. The copper which contained silver had previously been reduced 10 per cent in area and the other specimens 7 per cent in area.

These investigators also studied the behavior of arsenical and silver-arsenical copper at 300 and 350 °C under compression at 7,800, 11,100, and 16,800 lb/in.<sup>2</sup> The silver-arsenical copper was deformed less than the arsenical copper at the high and low loads, but comparatively little difference was noted in the two kinds of material for 11,100 lb/in.<sup>2</sup>

Table 10.—Creep Values of Arsenical and Silver-arsenical Coppers at 300 °C.<sup>16</sup>

Material	Stress (lb/in. <sup>2</sup> )	Approximate initial strain (in./in.)	Approximate minimum rate of strain in./in./day	Duration of test (days)
Arsenical	11,200	0.0019	0.00206	4B <sup>a</sup>
	9,000	.0016	.00056	12B
	6,700	.0006	.00014	49B
Silver-arsenical	11,200	.0009	.00037	7.5B
	9,000	.0007	.000091	26B
	6,700	.0006	.000020	42U <sup>b</sup>

<sup>a</sup>B = broken.

<sup>b</sup>U = unbroken.

Tapsell and Johnson<sup>16</sup> conducted creep tests on arsenical copper containing about 0.33 per cent of arsenic and on silver-arsenical copper containing a like amount of arsenic and about 0.07 per cent of silver. Table 10 contains their data for tests at 300 °C on material previously annealed at 350 °C.

According to Bassett<sup>18</sup> the presence of 0.06 per cent of silver calls for increasing the annealing temperature from 250 to 350 °C for work in the rolling mill.

An interesting observation on the effect of silver on electrolytic copper used for castings has been made by Ash.<sup>19</sup> By using the spiral-casting method developed by Saeger and Krynitsky<sup>20</sup> for testing the fluidity of molten metals, Ash found that, while copper containing 0.04 or 0.10 per cent of silver did not produce as long a spiral as copper alone, yet it filled the mold better and gave a much sharper corner, which suggested a decreased surface tension.

This matter was also investigated by the Project, since Ash<sup>19</sup> apparently did not take into consideration the effect of oxygen. The tests were repeated, using electrolytic copper and double refined silver, melted in a graphite crucible by high-frequency induction under a preheated charcoal cover. The data obtained are summarized in Table 11, the analyses being made on samples cut from the fluidity spiral. The electrolytic copper used contained 0.002 per cent silver and 99.951 per cent copper by analysis. No significant effect seems to have been produced

Table 11.—Effect of Silver on the Fluidity of Copper.

Composition (%)	Casting Temperature (°C)	Length of Saeger Spiral (inches)
0.002 silver, 0.04 oxygen	1137	5.4
	1137	4.5
0.08 silver, 0.04 oxygen	1137	4.5
1.09 silver, 0.01 oxygen	1140	4.0
0.002 silver, 0.08 oxygen	1300	20.5
	1300	23.9
1.09 silver, 0.01 oxygen	1280	25.7

at the lower casting temperature, although the fluidity of the 1.09 per cent silver alloy cast at 1300 °C appears to be somewhat superior to that of the control.

Table 12 summarizes data obtained by the Project on the physical properties of silver containing 7.5 per cent copper. Samples of sterling silver 0.057 inch thick were heated for one hour at 760 °C and then quenched in water. The quenched alloy had a Rockwell F hardness of 46; on aging for 30 minutes at 300 °C the hardness increased to 99. The manufacture of sterling silver and its physical properties have been discussed in some detail by Sperry,<sup>21</sup> Smith and Turner,<sup>22</sup> Leach and Chatfield.<sup>23</sup> According to the last-named authors, 1200 °F (648 °C) is a suitable temperature for annealing sterling silver. Unless protection from oxidation is provided, heating sterling in air to such a temperature will produce a copper oxide scale.

Table 12.—Physical Properties of Sterling (7.5 per cent Copper) Silver Sheet.

Condition	Vickers Hardness	Tensile Strength p. s. i.	Yield Strength <sup>3</sup> p. s. i.	Elongation % in 2"	Resistivity Microhm-cm 20 °C
Annealed <sup>1</sup>	56	39,300	22,900	42	2.1
Cold-rolled <sup>2</sup>	119	54,000	51,700	12	2.3

<sup>1</sup> Heated for one hour at 760 °C (1400 °F) and quenched in water. No. 15 B. & S. gauge.

<sup>2</sup> Cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge.

<sup>3</sup> 0.2% offset method.

Smith<sup>24</sup> gives the data appearing in Table 13 on the thermal conductivity of copper-silver alloys. For comparison, the thermal conductivity of pure silver is 1.00 and of pure copper 0.92.

2. *Electrical.*—The electrical conductivity of copper is altered surprisingly little by the addition of small percentages of silver. Data quoted by Gregg<sup>8</sup> indicate that the presence of 0.1 per cent silver lowers the conductivity by only 0.7 per cent, whereas the same percentage of arsenic lowers it about 25 per cent.<sup>25</sup> Norbury<sup>11</sup> has shown that silver has the least effect of all the metals in lowering the conductivity of copper, and according to Johansson and Linde,<sup>26</sup> the conductivity of the silver-

Table 13.—Thermal Conductivity of Copper-Silver Alloys <sup>24</sup>

Copper (%)	Silver (%)	Thermal Conductivity at 62 °C (c. g. s. units)
95	5	0.777
90	10	.723
80	20	.639
70	30	.628
60	40	.658
55	45	.751
50	50	.747
45	55	.749

copper series does not fall below 75 per cent of that of copper for any composition in the series, all the specimens being in the hard condition. For alloys annealed for 100 hours at 350° C, the conductivity did not fall below 90 per cent of that of annealed copper.

3. *Chemical.*—There is very little published information on either atmospheric or chemical corrosion of argentiferous copper. Experiments at the United States Naval Engineering Experiment Station on the corrosive action of brackish river water (5,500 ppm of chlorine) on copper containing 5 per cent silver indicated no superiority to ordinary copper. Red brass (15 per cent zinc) containing 1 or 5 per cent silver showed considerably more corrosion damage than corresponding alloys containing no silver.

It is claimed (U. S. Patent 2,188,681) that a fractional percentage of silver is effective in preventing dezincification of brass.

The copper-silver alloys high in silver are seldom employed for chemical applications requiring a high resistance to corrosion, as the presence of the copper-rich phase reduces the corrosion resistance when compared to that of fine silver (which does not contain in excess of 0.1 per cent of copper). The properties of sterling silver (92.5 per cent minimum silver, remainder usually copper) are well known, and it is generally found that the susceptibility of sterling silver to tarnish is greater than that of pure silver. However, for some special applications the corrosion resistance of the alloys containing up to 10 per cent of copper (coin silver) is adequate and the mechanical properties much better than those of pure silver.

### (c) Applications

Silver-rich alloys of the silver-copper series have long been of great importance because of their use in coinage and sterling ware. Coin silver (10 per cent copper) also finds use in electrical contacts. However, the possibility of improving copper by the addition of small percentages of silver has not been seriously considered until rather recently. This material has been found particularly useful when soldering is involved, since the heat of soldering does not cause undue softening of the metal. Commutator bars are frequently made of a similar alloy to insure that their hardness will be maintained when warmed. Photoengraving plates

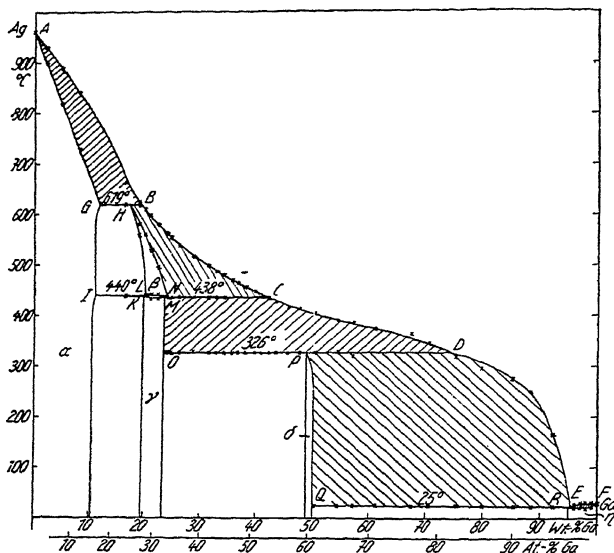


FIGURE 19. Gallium-silver constitutional diagram.  
Weibke, Meisel, and Wiegels: *Z. anorg. allgem. Chem.*, **226**, 201 (1936).

of copper may also have a fractional percentage of silver to prevent softening of the cold-rolled sheet during processing at an elevated temperature. A welding rod for copper much in favor with coppersmiths contains about 1 per cent of silver, the remainder being copper plus a trace of deoxidizer. A small proportion of silver, usually less than 1 per cent, is used in commercial high-conductivity copper alloys of various types; these alloys are usually not less than 95 per cent copper and contain small amounts of hardening elements such as chromium, beryllium, tin, cobalt, or cadmium. Silver-copper alloys form the basis of a series of brazing alloys, which usually contain substantial amounts of zinc, and lesser amounts of other elements such as cadmium and phosphorus (see Chapter 7). The low melting point and remarkable fluidity and capillary flow of the silver brazing alloys is of interest.

#### (a) Constitution 14. Gallium-Silver

Figure 19 is the constitutional diagram for gallium-silver alloys, according to Weibke, Meisel, and Wiegels.<sup>1</sup> The system was examined by thermal, micrographic, and x-ray methods. The  $\alpha$ -phase contains 12 per cent gallium at 619 °C, 11 per cent at 440 °C, and 10.4 per cent at room temperature; the  $\beta$ -phase extends from 12 to 17 per cent gallium at 619 °C and from 11 to 23.7 per cent gallium at 440-438 °C below

which temperature it is converted into the  $\gamma$ -phase ( $\text{Ag}_5\text{Ga}_2$ ) which is homogeneous in the range 19.6-23.5 per cent gallium but is not hexagonal like  $\text{Ag}_5\text{In}_2$ . The  $\delta$ -phase ( $\text{Ag}_2\text{Ga}_3$ ) is formed by a peritectic reaction at  $326^\circ\text{C}$  and has only a small range of homogeneity around 50 per cent gallium. The solid solubility of silver in gallium is about 5 per cent and the eutectic point is  $25^\circ\text{C}$ , 5% silver. Moeller<sup>2</sup> reports that the phase  $\text{Ag}_3\text{Ga}$  is isomorphic with  $\text{AgZn}$ .

### (b) Properties

According to Weibke, Meisel, and Wiegels,<sup>1</sup> the  $\alpha$ -alloys containing up to about 14 per cent of gallium resemble silver in their properties; they are malleable and soft, and have the white color of silver. After long standing in a laboratory atmosphere they acquired only a faint yellow tarnish. Alloys containing from 18 to 25 per cent of gallium are brittle and unworkable; their color resembles that of nickel-silver. Alloys containing 25 to 50 per cent of gallium are extremely brittle and resemble chromium in color. In the gallium-rich alloys, the gallium can be squeezed out like mercury from an amalgam.

### (c) Applications

Despite the interesting properties of the silver-rich and gallium-rich alloys of this system, no commercial application is known. The markedly

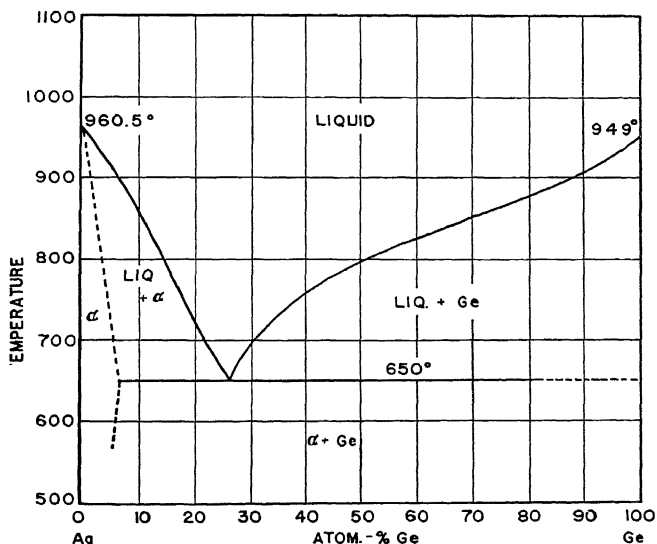


FIGURE 20. Germanium-silver constitutional diagram.

Briggs, McDuffie, and Willisford: *J. Phys. Chem.*, **33**, 1080 (1929).



lowered melting range of alloys containing about 10 per cent of gallium suggests the possibility of using gallium together with other suitable elements to produce low-melting alloys for brazing or soldering.

### 15. Germanium-Silver

#### (a) Constitution

Figure 20 is the constitutional diagram for germanium-silver alloys, according to Briggs, McDuffie, and Willisford.<sup>1</sup> A simple eutectiferous system is formed with about 6 to 7 atomic per cent of germanium soluble in silver just below the eutectic temperature, and no solubility of silver in germanium.

#### (b) Properties

Briggs, McDuffie, and Willisford,<sup>1</sup> observed that the alloys became less brittle as the silver content increased and that it was impossible to fracture the eutectic alloy in a mortar. Jordan, Grenell, and Herschman observed that samples containing 2, 4, and 6 per cent of germanium could be rolled, had a bright gray color, and inferior tarnish resistance.

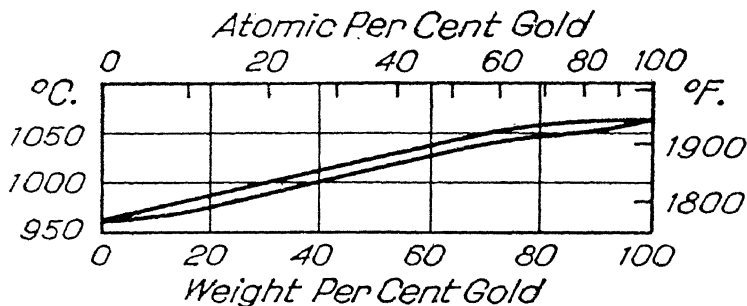


FIGURE 21. Gold-silver constitutional diagram.

Leach: A. S. M. Handbook, p. 1503 (1939).

#### (c) Applications

No commercial application is known, but because of the interesting properties of low silicon-silver alloys and the similarity between germanium and silver, further investigation of this system for precipitation hardening properties, etc., seems warranted.

### 16. Gold-Silver

#### (a) Constitution

Figure 21 is the constitutional diagram for gold-silver alloys according to Leach<sup>1</sup> based on the work of Broniewski and Wesolowski,<sup>2</sup> which is in good agreement with that of Sterner-Rainer.<sup>3</sup> The constitution of these alloys has been reviewed by Leach.<sup>1</sup> The alloys form an unbroken solid-solution series and all have a face-centered cubic lattice.

## (b) Properties

The properties of gold-silver alloys have been reviewed by Wise,<sup>4</sup> Sterner-Rainer,<sup>3</sup> and Crowell, Wise and Eash.<sup>5</sup> According to Wise,<sup>4</sup> the maximum strength of the annealed alloys is but 30,000 pounds per square inch. The 18-carat (75 per cent gold) alloy has an attractive green color. Further increase in silver content yields alloys of paler green. The 12-carat (50 per cent gold) alloy is an unattractive greenish-white and tarnishes readily. The tarnish resistance of alloys containing even 20 to 30 per cent of gold is poor. Table 14 gives the following properties for an 18-carat green gold alloy, containing 75 per cent gold, 25 per cent silver:

Table 14.—Physical Properties of Gold-Silver Alloys.<sup>4</sup>

Type	Composition—			State	Yield Point p. s. i.	Tensile Strength p. s. i.	Elonga- tion (%)	Brinell Hardness No.
	Au	(%) Ag	Cu					
18 carat, green	75.0	25.0	—	Annealed	Very low	27,000	36.1	32
				Cold rolled 60%	47,000	49,000	2.6	93
14 carat, green	58.3	35.7	5.8	Annealed and quenched	39,000	64,000	34.9	78
				Annealed and slowly cooled	39,000	64,000	34.9	78
				Cold rolled 60%	110,000	113,000	2.4	139

The table also includes some properties of a 14-carat green gold alloy, containing 58.3 per cent gold, 35.7 per cent silver, and 5.8 per cent copper.

The gold-silver-copper ternary alloys and modifications thereof have high physical properties and sufficient corrosion resistance to be of interest in the jewelry trade and the dental profession. The high-carat alloys of gold-silver-copper are solid solutions at elevated temperature, but may contain an ordered phase derived from AuCu at low temperatures. The low-carat alloys may contain some eutectic. The melting temperature is generally rather low, and the tarnish resistance depends principally upon the gold content. At 14 carat (58.3 per cent gold) the maximum strength in annealed material of 78,000 pounds per square inch is secured when equal quantities of silver and copper are present. The strength of the annealed 14-carat alloys of this type reaches a maximum at about 20 per cent copper, but the solidus temperature is only about 830 °C at this point. For this reason, care must be taken to avoid damage in soldering alloys of this type. The introduction of small percentages of palladium raises the melting point; it has been added to 12- and 14-carat alloys for this reason, and also to increase resistance to tarnish.

According to Jarrett,<sup>6</sup> when silver is present in any of the 10-carat gold alloys, the corrosion loss is greatly reduced. Silver tends to change the brass yellow color to a milder and softer yellow shade.

### (c) Applications

The principal uses for alloys of this type are in the jewelry trade, the dental profession, and to some extent for electrical contacts. The 75 per cent gold-25 per cent silver alloy is sometimes used for jewelry decorations because of its attractive green color. Some use has been made of 20- to 30-per cent gold alloys for electrical contacts. The 70-6-24 gold-platinum-silver alloy has been widely used for electrical contacts in telephone equipment. The dental profession uses large quantities of high-carat gold alloys containing as principal alloying constituents silver and copper. Palladium may be substituted for some of the gold to produce white gold. Strong yellow denture golds contain 60 to 70 per cent gold, together with 2 to 12 per cent of platinum or palladium to improve their properties. Dental alloys containing copper and the platinum metals, as well as many of the colored jewelry golds are age-hardenable. Further reference to dental alloys is made in Chapter 18. Special applications are occasionally made in the chemical industry for alloys of this general type.

## 17. Indium-Silver

### (a) Constitution

Figure 22 is the constitutional diagram for indium-silver alloys, according to Weibke and Eggers.<sup>1</sup> These investigators used thermal, micrographic and x-ray methods. Their results are in good agreement with those of Hume-Rothery, Mabbott, and Evans.<sup>2</sup> According to Goldschmidt,<sup>3</sup> the  $\delta$ -phase has a close-packed hexagonal structure. Frevel and Ott<sup>4</sup> studied the structure of the intermediate phases of this system.

### (b) Properties

Because of its white color and resistance to tarnish, indium has been considered as a coating, or alloying ingredient, for silver (U. S. Patent 1,847,941). Raub and Schall<sup>5</sup> examined the properties of silver-indium alloys and indium coatings on silver, and concluded that the specimens showed no advantage over existing alloys as regards either wear or corrosion properties. Raub and Roters<sup>6</sup> established that small indium contents do not appreciably affect the workability or tarnishing properties of silver or silver-copper alloys. Indium in excess of 20 per cent materially reduces the workability of the alloys and promotes hot-shortness. Indium reduces the resistance of silver to acids, although not so much as does copper. They concluded that indium additions are of no advantage for increasing the resistance of silver to acids or tarnish. Jarrett<sup>7</sup> reports a small increase in hardness of quenched and aged alloys containing 1 to 4 per cent of indium, and that indium in this range lowers the conductivity materially.

Smart<sup>8</sup> describes tests on indium-plated cadmium-silver bearings, showing that such bearings, unlike the regular cadmium-silver bearings,

were not corroded by hot lubricating oil containing 0.5 per cent of oleic acid.

### (c) Applications

Indium may be used to increase the corrosion-resistance of cadmium-silver bearings. Several patents have been issued, claiming indium-silver alloys of improved resistance to tarnish (U. S. Patents 1,847,941 and 1,934,730). Some possible use may be found in dental alloys according to U. S. Patents 1,963,085; 1,965,012 and 1,987,451.

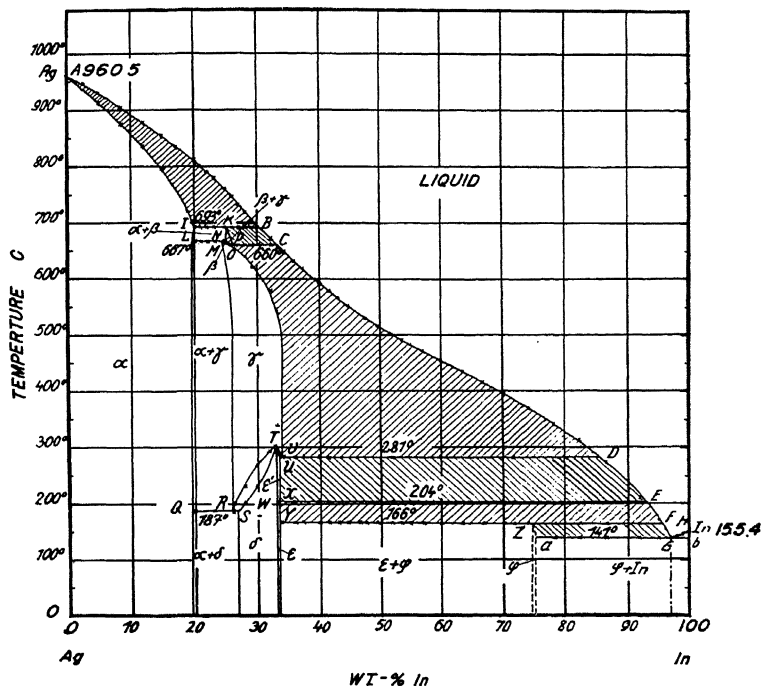


FIGURE 22. Indium-silver constitutional diagram.

Weibke and Eggers: Z. anorg. allgem. Chem., 222, 145 (1935).

## 18. Iridium-Silver

(a) **Constitution**

According to Rossler,<sup>1</sup> iridium does not dissolve in molten silver. The procedure used by Rossler, however, was not one that would suffice to disclose limited solubility.

### (b) Properties

Downie<sup>2</sup> claims that tarnishing and discoloration of silver can be prevented by the introduction of small proportions of metals of the platinum group—namely, platinum, rhodium, and iridium—in the alloy deposited from baths containing nitrites and hyponitrites, or other salts of “hypo” acids of the platinum metal group. The deposits are whiter than chromium plate.

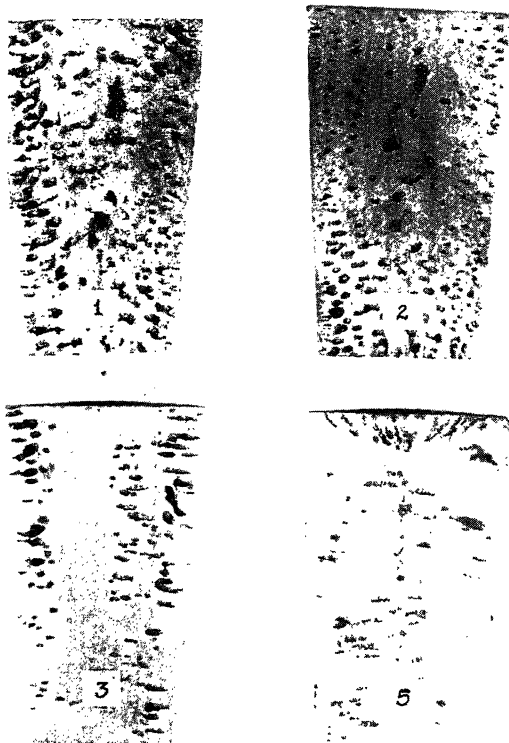


FIGURE 23. Influence of silver on porosity of Armco iron ingots.

Alloy 1. No silver added.  
Alloy 2. 0.025% silver added.

Alloy 3. 0.025% silver added.  
Alloy 5. 0.25% silver added.

### (c) Applications

According to Downie,<sup>2</sup> silver alloy plating of the type discussed above has found application in microscope reflectors.

## (a) Constitution

## 19. Iron-Silver

Petrenko <sup>1</sup> reported that silver and iron are insoluble in the molten state at a temperature of 1600 °C. On cooling the molten mixture slowly, the metals separate into two layers. Tammann and Oelsen <sup>2</sup> have used a very sensitive magnetic method in studying the solubility of iron in silver and state that about  $5 \times 10^{-4}$  per cent of iron is retained in solution in silver. Silver is not at all soluble in iron, according to Wever.<sup>3</sup> Fink and de Marchi <sup>4</sup> claim to have found that between 0.5 and 1 per cent of silver dissolved in iron prepared by sintering the powdered metals. Dornblatt <sup>5</sup> has discussed the work of Fink and de Marchi and presented data indicating a solubility of silver in Armco iron and in cast steel of less than 0.01 per cent. Burgess and Aston <sup>6</sup> reported that electrolytic iron would retain a maximum of 0.69 per cent of silver; the author believes this figure is a measure of the mechanically included silver, entrapped in the solidifying ingot.

## (b) Properties

Stodardt and Faraday <sup>7</sup> state that a tool-steel alloy containing 0.2 per cent of silver was "decidedly superior to the very best (edge) steel, and this excellence is unquestionably owing to combination with a minute portion of silver."

Tammann and Ruhenbeck <sup>8</sup> observed that, in a hydrogen atmosphere, a drop of liquid silver would wet electrolytic iron at a sufficiently high temperature, and after cooling could be only partially removed with the aid of a sharp chisel. Dornblatt <sup>5</sup> presented data based on studies undertaken in coöperation with Briggs and Taylor indicating that, although less than 0.01 per cent of silver is retained in Armco iron, the addition of 0.05 to 0.25 per cent of silver to the molten iron reduces blow-hole porosity in the ingot. Figure 23 shows the influence of silver additions on small ingots of Armco iron and Table 15 summarizes data on the analyses of the heats studied.

Table 15.—Analyses of Iron-Silver Alloys.

Alloy	C (%)	Mn (%)	Si (%)	Al (%)	Oxygen (%)	Silver Retained (%)	Silver Added (%)
1. Armco Iron	.062	.03	.04	nil	.073	—	—
2. Armco Iron	—	—	—	—	—	0.007	0.025
3. Armco Iron	—	—	—	—	—	0.004	0.050
4. Armco Iron	.056	.01	.02	nil	.093	0.002	0.05
5. Armco Iron	—	—	—	—	—	0.061	0.250
6. Armco Iron	.060	.01	.02	nil	.110	0.002	0.50
7. Cast steel	0.30	—	—	—	—	0.005	1.0

As the effect noted was observed on a second group of ingots, similarly prepared, and the analyses fail to show significant differences in the amount of deoxidizing elements present, it is concluded that the reduction in porosity was an effect of the additions of silver. Silver in the molten

state at atmospheric pressure can dissolve 20 times its own volume of oxygen. Since the added silver was still liquid at the time when the iron had begun to solidify, it may have dissolved oxygen which the solidifying iron was evolving. By the time the silver solidified, it had largely been forced into the shrinkage cavity, or else had settled to the bottom of the ingot. The tendency of silver to liberate its dissolved oxygen upon solidification would not result in blow-holes in the steel either because the silver liberated the oxygen where it could do no harm or because the rigidity of the steel at the freezing temperature of silver (960 °C) is sufficient to restrain the formation of a gas bubble emanating from a globule of silver.

Fink and deMarchi prepared ingots of iron and silver containing from 0.25 to 50 per cent of silver from mixed powders sintered at 950 °C in an oxygen-free hydrogen atmosphere, and were able to work the ingots down into thin sheets. They determined the electrical resistivity and resistance of these alloys to corrosion by hydrochloric and acetic acids, and reported an improvement in the corrosion resistance of the samples containing about 1 per cent of silver. De Marchi tested samples of the alloys prepared by Briggs and Taylor in a 3 per cent sodium chloride solution and obtained the data of Table 16. Kinzel<sup>9</sup> stated,

Table 16.—Corrosion of Iron-Silver Alloys in 3 per cent Sodium Chloride Solution\*

Alloy	Sample Weight (gm)	Loss (gm)	mg/cm <sup>2</sup> /yr
Armco Iron	30.4258	1.3541	680
0.002 Ag, Rem. Armco Iron	32.7027	1.5523	757
0.002 Ag, Rem. Armco Iron	32.1591	1.4823	722
0.005 Ag, 0.30 C.			
Rem. Armco Iron	17.5338	0.6244	579

\*Intermittent immersion, 3 weeks. Averages of 3 tests reported.

"The addition of silver to iron containing silicon has shown that the alpha-forming tendency of the silicon is at least partially offset by the presence of the silver, leading to the natural conclusion that silver is soluble to some degree in iron and is an austenite-promoting element analogous to copper."

Norton<sup>10</sup> discusses the very interesting results obtained by Norton, Kaye, Williams, Uhlig, and Wulff of the Massachusetts Institute of Technology under sponsorship of the Chemical Foundation, Inc. These results are discussed in U. S. Patent 2,156,914 in the following terms:

"We have discovered that the addition of small quantities of silver to stainless steel containing chromium and nickel, particularly the 18-8 stainless, increases its resistance to pit corrosion and gives it other valuable properties hereinafter fully discussed. . . . the invention is primarily useful with alloys in which the percentages of chromium and nickel or the equivalent approximate 18 and 8 respectively. . . . we have been unable to discover any metal except silver which has all of its valuable

properties when combined as described, although a combination of molybdenum and silver affords some unexpectedly favorable consequences.

"Comparative total immersion tests in acidified ferric chloride solution (a very severe pitting medium for stainless steel of this general type) have shown that....the pit corrosion produced by equal periods of immersion is only about 16% of that of a standard 18-8 stainless steel without silver.

".....to obtain the beneficial effects on our invention it seems to be necessary that nickel or manganese shall be present as well as the silver to accomplish solution of the silver, and reduce the amount of segregation of silver at the grain boundaries.

"These facts.....afford an explanation of the singular resistance of chrome-nickel-silver stainless steel to pitting when exposed to sea water. ....the entire surface of the metal—the grain as well as the grain boundary—contains silver, the water-insoluble self-healing film of silver chloride forms over the entire surface of the metal, protecting it, instead of leaving the grains themselves exposed to the electrolytic effect of the sea water if there is a difference of potential due to a difference in oxygen concentration. This continuous self-healing film of chloride covering the entire surface of the metal forms an effective protecting layer which prevents further attack at any point within the area covered by the coating.

".....tests which we have made gave a heat conductivity of stainless steel....of .053 c. g. s. units per second, whereas tests, made with the same apparatus and under the same conditions, of a standard 18-8 stainless steel without silver but otherwise of very nearly the same analysis, gave only .042 c.g.s. units per second.....

".....We have found....that a piece of ordinary 18-8 stainless steel work-hardens so much after one or two strokes of a jeweller's hack-saw that the saw will not cut it effectively afterwards, while a similar piece of metal of our novel alloy may be cut completely through by the use of a single blade.

"When turned in a lathe ordinary 18-8 stainless steel forms a springy continuous chip which is likely to wind itself around the tool or the work and interfere with the machining operation. The alloy embodying our invention turns in about the same manner as ordinary cold-rolled steel.

"Steel embodying our invention can be given a better surface polish than comparable steels and this can be done with much less difficulty. This property enhances the corrosive resistance of the metal, as polishing tends to render the surface of the material more uniform and therefore less susceptible to electrolytic action.

"It is possible also that our alloy may have a toxic effect and therefore tend to kill or discourage the growth of water organisms which might otherwise adhere to the surface of the metal and cause areas of different oxygen concentration.



".....it is believed that the most useful and practical proportion ranges of the several elements are substantially as follows: carbon, not more than 1%, chromium 6% to 20%, nickel and/or manganese 20% to 0.50%, and silver in effective amounts up to 1% in case of nickel and up to 2% in case of manganese, and to which may be added molybdenum up to 4%."

Table 17 gives the range of composition of some alloys discussed in the patent.

Table 17.—Composition of Stainless Steel Alloys Containing Silver  
(U. S. Patent 2,156,914)

	C (%)	Ni (%)	Cr (%)	Mn (%)	Mo (%)	Ag (%)
For resistance to pit corrosion	.06-.16	8-11.50	18.00-18.27		3.00-4.00	0.15-0.42
For high surface polish	0.16	8.00	18.00			0.50
For high thermal conductivity	0.07	9.42	19.32	0.12		0.14

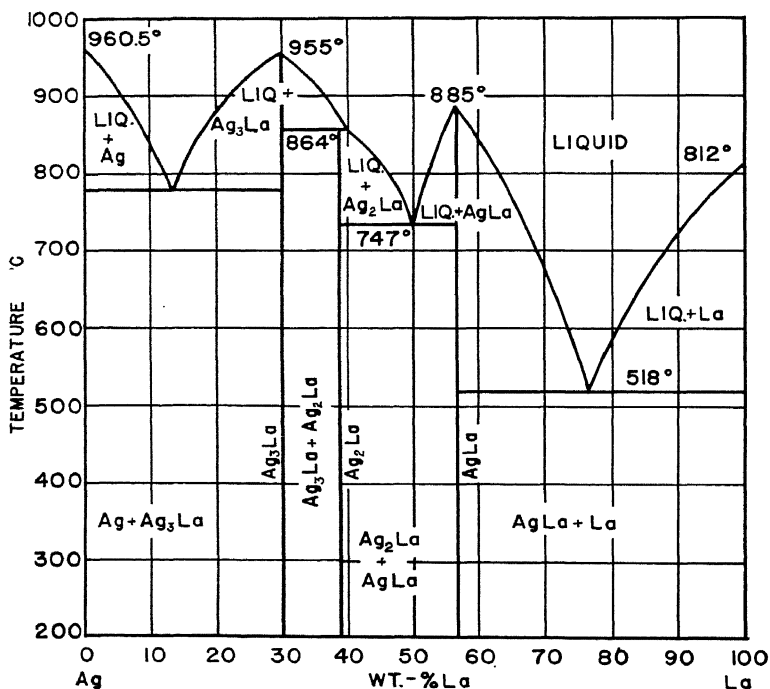


FIGURE 24. Lanthanum-silver constitutional diagram.

Cannari: Metallurgia Italia, 23, 802 (1931).

### (c) Applications

The use of small additions of silver in stainless steel is now being commercialized. Such applications have been discussed in a number of recent articles.<sup>11-18</sup> U. S. Patents 1,757,508; 1,838,180; 1,969,705; 2,156,914; 2,172,388 and 2,172,422 refer to ferrous alloys, rich in nickel or chromium, containing silver. British Patent 324,009 (1928) and a recent German Patent (658,635) also relate to such alloys.

## 20. Lanthanum-Silver

### (a) Constitution

Figure 24 is the constitutional diagram for lanthanum-silver alloys, according to Canneri.<sup>1</sup> The liquidus and solidus curves were located by thermal and microscopic methods. The solubility relationships in the solid state were not investigated.

### (b) Properties

Canneri<sup>1</sup> compares the pyrophoric properties of lanthanum-silver alloys with the pyrophoric behavior of lanthanum-copper alloys. The lanthanum-silver alloys are less inflammable than the corresponding lanthanum-copper alloys, and there is a narrower range of composition for the alloys possessing inflammability.

### (c) Applications

No commercial applications of lanthanum-silver alloys appear to have been made.

## 21. Lead-Silver

### (a) Constitution

Figure 25 is the constitutional diagram for lead-silver alloys prepared by the Project, based on the work of Heycock and Neville,<sup>1</sup> Friedrich,<sup>2</sup> Petrenko<sup>3</sup> and of Chiswik and Hultgren.<sup>4</sup> According to the latter investigators, 1.3 per cent of lead is soluble in silver at 300 °C, and only 0.6 per cent at 250 °C. Seith and Keil<sup>5</sup> state that the limit of solid solubility of silver in lead is almost a linear curve falling from about 0.1 per cent of silver at the eutectic temperature to about 0.05 per cent of silver at 200 °C. The constitution of lead-silver alloys has been reviewed by Dornblatt.<sup>6</sup> The eutectic occurs at 304 °C and 97.5 per cent of lead.

### (b) Properties

1. *Physical.*—Russell<sup>7</sup> studied the recrystallization of cold-worked lead containing relatively small proportions of silver. To lead containing less than 0.0005 per cent of impurities, he added silver in various amounts to produce very pure alloys which were cast and annealed *in vacuo*, then distorted and the period required for recrystallization to be completed was noted. The results are summarized in Table 18.

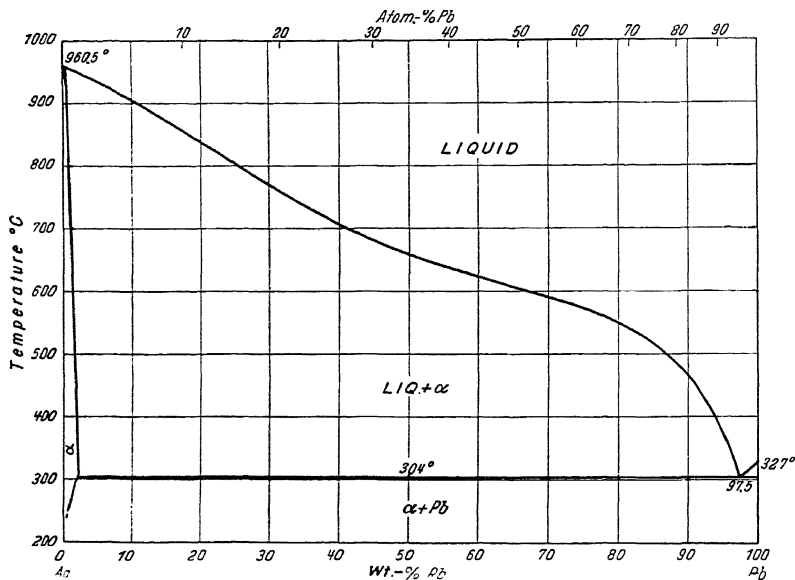


FIGURE 25. Lead-silver constitutional diagram.

Chiswick and Fultren: *Metals Tech.*, TP 1169, April, 1940.Petrenko: *Z. anorg. allgem. Chem.*, 53, 202 (1907).Friedrich: *Metallurgie*, 3, 396 (1906).Heycock and Neville: *J. Chem. Soc.*, 65, 72 (1894).

The effect of small percentages of silver on the rate or temperature of recrystallization of lead has been noted also by Beck,<sup>8</sup> Jenckel and Poetsch,<sup>9</sup> and by Hofmann and Hanemann.<sup>10</sup> Greenwood and Worner,<sup>11, 12</sup> Greenwood,<sup>13</sup> Russell,<sup>14</sup> and McKeown<sup>15</sup> discuss the increase in creep strength and resistance to deformation of lead produced by very small proportions of silver.

Table 18.—Effect of Small Percentages of Silver on the Recrystallization of Lead.<sup>7</sup>

Added silver (%)	Distortion (%)	Temperature during recrystallization (°C)	Time for recrystallization
none	5	Room temperature	5 minutes
0.0001	5	Room temperature	24 hours
.0005	5	Room temperature	60 days
.005	5	125	20 hours

The density of the alloy varies substantially linearly with composition, according to the work of Matthiessen,<sup>16</sup> Spencer and John,<sup>17</sup> Stephens and Evans.<sup>18</sup> Matthiessen<sup>16</sup> also measured the conductivity of lead-silver alloys; and Spencer and John<sup>17</sup> and Stephens and Evans<sup>18</sup> measured their magnetic susceptibility.

Ludwik<sup>19</sup> measured the hardness of lead and three lead-silver alloys with an Amsler machine using a 90-degree cone, his results being given in Table 19.

Table 19.—Hardness of Some Silver-Lead Alloys.<sup>19</sup>

Silver (%)	—Hardness*—	
	As quenched	Annealed at 300 °C for 2 to 3 hours
0.0		About 5
0.5	9.5 to 9.8	10.0 to 10.6
1.0	10.3 to 11.4	11.2 to 11.4
2.0	11.0 to 12.0	12.3 to 12.5

\*Ratio of load to projected area of indentation.

Some data obtained by the project on lead and lead-silver alloys are summarized in Table 20.

Table 20.—Physical Properties of Some Lead and Lead-Silver Alloys.

Composition	Vickers Hardness Number			Tensile Strength p. s. i.—		Elongation —% in 2"—		Resistivity —microhm-cm—	
	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>
Pure lead	3.91	4.22	3.63	1,920	2,195	35.0	21.0	20.8	21.1
Pb+2.82% Ag	6.47	7.88	11.50	3,780	3,870	24.0	25.0	19.3	19.5
Pb+4.68% Ag	5.96	6.85	9.59	3,820	4,095	15.0	26.5	19.1	18.1

<sup>1</sup> No. 15 B. & S. gauge, annealed 1 hour at 250 °C.

<sup>2</sup> Cold-rolled from No. 15 B. & S. to No. 18 B. & S.

<sup>3</sup> Cold-rolled from  $\frac{3}{4}$ " thick chill-cast ingot to No. 15 B. & S.

Johnson<sup>20</sup> has studied the soldering properties of lead-silver alloys and found that an alloy of lead with 5 to 6 per cent of silver has useful properties as a solder for joints exposed to somewhat elevated service temperature. The properties of the 6 per cent silver alloy are compared with those of a 50-50 lead-tin solder in Table 21, based on Johnson's

Table 21.—Comparison of Lead-Silver and Lead-Tin Alloy Solders.<sup>20</sup>

Composition	Melting Range (°F)	—Shear Strength p. s. i.—	
		70 °F	350 °F
94 Pb—6 Ag	570–700	2470	1556
50 Pb—50 Sn	370–450	2580	441

data.<sup>20</sup> The following data, which were obtained at National Bureau of Standards by A. R. Maupin, Research Associate for the Copper and Brass Research Association, are of interest:

Table 21a.—Elevated Temperature Properties of Soldered Joints in Copper Tubing.

Temp. (°F)	Duration of Test (hours)	—Maximum shear stress which did not cause failure by creep p.s.i.—	
		4.68% Ag—95.3% Pb solder	50% Pb—50% Sn solder
85	9000	800	235 <sup>1</sup>
250	10,000	220	80 <sup>1</sup>
325	10,000	105	...

<sup>1</sup> Investigation of strength of soft soldered joints in copper tube plumbing. A. R. Maupin, National Bureau of Standards Building Materials and Structures series, 1940.

The superiority of the lead-silver alloy is quite apparent. Furthermore there was no deterioration at the bond at the end of the 325 °F test, such as has been noted in the case of solders having a constituent which diffuses readily into copper under these conditions. The lead-silver joints were fluxed with killed muriatic acid (zinc chloride) free from ammonium chloride, as the latter seems to have a slight adverse effect on the fluidity of the solder. According to Silberstein,<sup>21</sup> the 2.5 per cent silver-lead alloy to which 0.25 per cent of copper has been added is a useful solder for applications requiring a higher melting point than that of lead-tin solders.

2. *Chemical*.—It was demonstrated by Fink and Pan<sup>22, 23</sup> that the addition, even in small amounts, of lead to a silver anode or silver to a lead anode used in the electrolysis of sodium chloride, reduced the voltage required and also the corrosion of the anode. Additional work on an alloy containing 61 per cent of silver, reported by them to be the best composition for the purpose, has been carried out by Rabinovich and Rubanchik<sup>24</sup> and Zhivotinskii.<sup>25</sup>

In the attempt to find alloys of lead more resistant to sulfuric acid than pure lead, Garre and Mikulla<sup>26</sup> added  $\text{AgCd}_4$  in proportions up to 2 per cent, by weight, of the compound. They reported a considerably decreased loss of weight in both dilute and concentrated acid. At 100 and 200 °C, the loss of weight was markedly less for the alloy than for lead. Lead-silver anodes for chromium plating are discussed by Ishida.<sup>27</sup> Tainton<sup>28-31</sup> has developed the use of lead containing 1 to 2 per cent of silver for insoluble anodes now widely used in producing electrolytic zinc of high purity. The behavior of lead-silver alloys as anodes in sulfuric acid solution has also been investigated by Hanley, Clayton, and Walsh,<sup>32</sup> Rey, Coheur, and Herbiet,<sup>33</sup> Rey and de Rycker,<sup>34</sup> Larsen,<sup>35</sup> Pletnev and Soboleva,<sup>36</sup> and Combri and Pintelli.<sup>37</sup> According to Tainton, Taylor, and Ehrlinger<sup>30</sup> the addition of 0.5 to 1 per cent of silver to the lead used in making anodes for the production of electrolytic zinc produced metallic zinc of much lower lead content than when pure lead anodes were employed. Another advantage of the lead-silver anode is the by-product formation of a purer grade of manganese dioxide than was otherwise obtainable (U. S. Patent 1,759,493).

### (c) Applications

Two lead-silver solders have been employed to some extent; the 5 per cent silver—95 per cent lead alloy is one, and the other is the solder containing 2.5 per cent of silver, 0.25 per cent of copper, and 97.25 per cent of lead described by Silberstein.<sup>21</sup> The principal advantage of these solders is that they melt at a higher temperature than ordinary lead-tin solder. The Project has suggested that lead-silver alloys containing from 2.5 to about 5 per cent of silver be considered for use in the canning industry for two reasons: (a) at prevailing market prices the metal value of the lead-2.5 per cent silver alloy, for example, is less than that of lead-tin solders containing 25 per cent or more tin; and (b) the use of

the higher-melting lead-silver solder removes restrictions imposed by the low melting point of lead-tin solder on the temperature which can be used for baking the can lining. The use of higher baking temperatures would permit a greater latitude in selection of the organic material to be used as a lining for the can. Reference to Figure 26, which is a chart showing the relation between solder composition and metal value in the solder, enables one to see clearly how the reduced price of silver has placed lead-silver solders in a favorable economic position. On Figure 26 has been plotted the metal value of solders of the various compositions based on prices as of February, 1940.

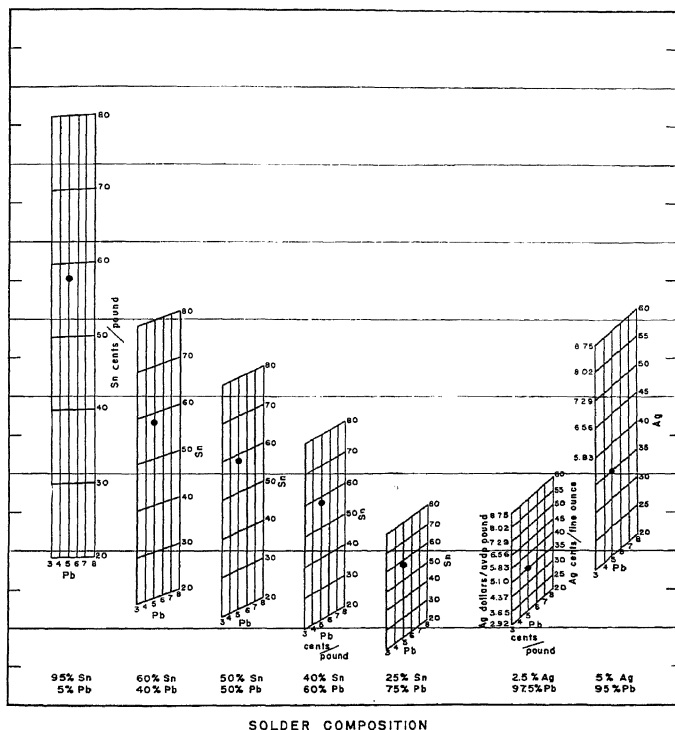


FIGURE 26. Relation between solder composition and metal value in the solder.

The use of lead-silver alloys as anodes in the production of electrolytic zinc is an application of importance.

According to U. S. Patents 2,057,604 and 2,099,551, the presence of from 1 to 3 per cent of lead in the form of the oxide constitutes an

improvement in silver switch contacts, by eliminating sticking and arcing. Some use is being made of such contacts.

### (a) Constitution

## 22. Lithium-Silver

Figure 27 is the constitutional diagram for lithium-silver alloys, according to Pastorello,<sup>1</sup> who prepared the alloys under an argon atmosphere in an austenitic stainless steel crucible. He reported a compound AgLi at 6.04 weight per cent lithium, and another compound, probably AgLi<sub>3</sub>, according to Perlitz.<sup>2</sup> Zintl and Brauer<sup>3</sup> confirmed the existence and CsCl type structure of AgLi, which is not stable at ordinary temperature.

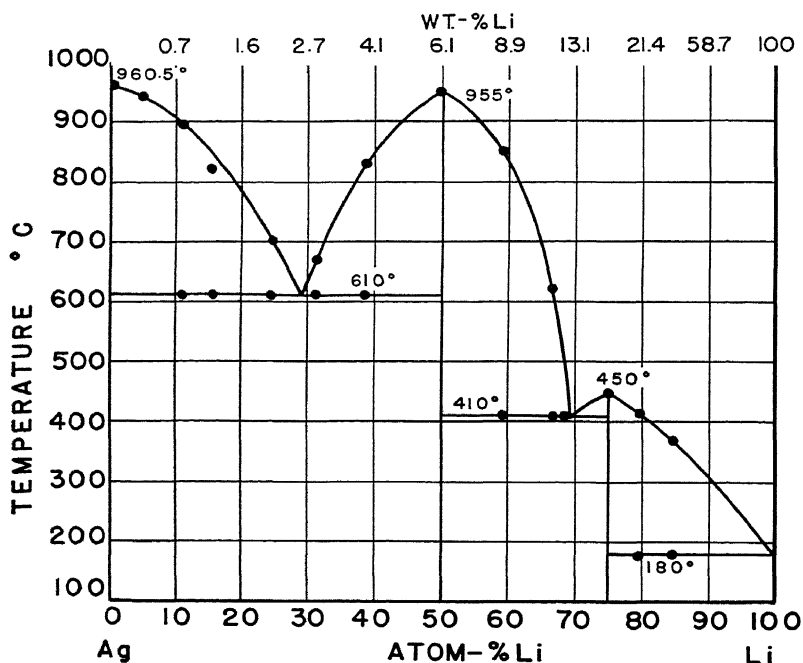


FIGURE 27. Lithium-silver constitutional diagram.

Pastorello: Gazz. chim. ital., 61, 47 (1931).

### (b) Properties

Briner and Wakker<sup>4</sup> studied the effect of using electrodes composed of copper or silver alloyed with the alkaline and alkaline-earth metals on the fixation of nitrogen in the arc. They report improvement in the process as a consequence of using electrodes of this type.

According to U. S. Patent 1,970,318, the inclusion of small proportions of lithium in silver-tin alloys increase their tarnish-resisting properties.

### (c) Applications

No application of importance is known.

### (a) Constitution

#### 23. Magnesium-Silver

Figure 28 is the constitutional diagram for magnesium-silver alloys, based on the work of Payne and Haughton<sup>1</sup> and Schemtschuschny.<sup>2</sup> It is probably correct for the magnesium-rich alloys, but is incomplete at the silver end. Smirnow<sup>3</sup> shows a range of solubility of about 4 per cent for the beta-phase. Ageew and Kutznetsov<sup>4</sup> used x-ray methods to determine the structure and limits of composition of all four phases of the magnesium-silver system.

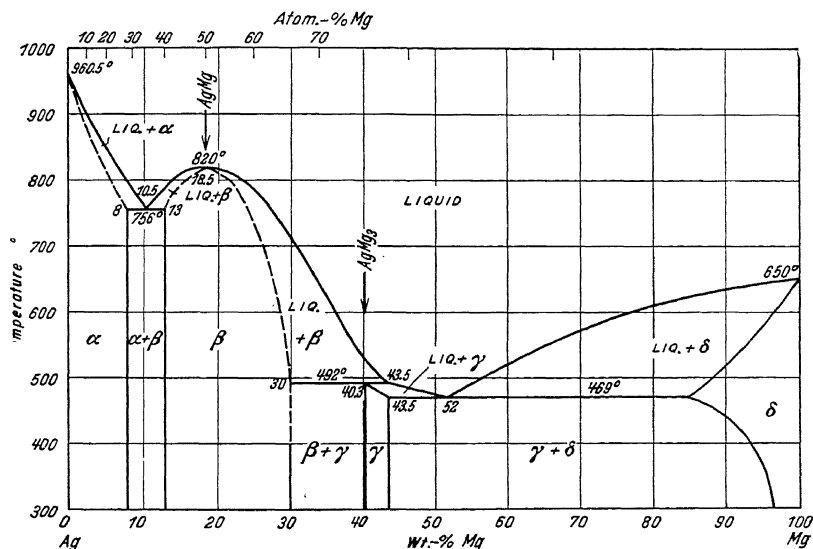


FIGURE 28. Magnesium-silver constitutional diagram.

Payne and Haughton: J. Inst. Metals, 80, 351 (1937).

Schemtschuschny: Z. anorg. allgem. Chem., 49, 400 (1906).

The alpha-phase is a solid solution of magnesium in silver reaching as far as approximately 72 atomic per cent silver. The body-centered beta-phase extends from 47 to 55 atomic per cent silver. The beta-phase may be regarded as consisting of solid solutions of silver and magnesium



in the compound  $\text{AgMg}$ . The gamma-phase consists of a solid solution of magnesium in the compound  $\text{AgMg}_3$  and has a homogeneity region extending from 20.5 to 25 atomic per cent silver. The phase has a structure belonging to the hexagonal system with 8 atoms per unit cell. The delta-phase is a solid solution of silver in magnesium and has a close-packed hexagonal structure. The solid solubility changes from 0.2 to 3.0 atomic per cent silver on raising the temperature from 260 to 440 °C. According to Hume-Rothery and Butchers,<sup>5</sup> the solid solubility of silver in magnesium is 15.3 per cent (3.9 atomic per cent) at the eutectic temperature (471 °C), and decreases with decreasing temperature to 3.9 per cent (0.9 atomic per cent) at 300 °C.

### (b) Properties

McDonald<sup>6</sup> has studied the mechanical properties of magnesium-silver alloys annealed at 450 to 850 °F, and age-hardened at 400 °F. He found no age-hardening under these conditions, for an unascertained reason. Nevertheless, silver produced good properties when added to magnesium, as shown in Table 22.

Table 22.—Properties of the Best Alloys of the Magnesium-Silver System.<sup>6</sup>

Properties	Ductility 4% Ag		Strength 12% Ag		Both 8% Ag	
	Annealed	Cold-rolled	Annealed	Cold-rolled	Annealed	Cold-rolled
Elongation (%)	20	—	9	—	16	—
Yield strength, 1000 p. s. i.	22	35	27	39	25	38
Tensile strength, 1000 p. s. i.	35	41	41	48	39	45

Haughton and Prytherch<sup>7</sup> prepared forged magnesium-silver alloys containing 2 and 6 per cent of silver and found that silver increased the ultimate strength of magnesium at temperatures up to 290 °C. They prepared an alloy containing 2 per cent of silver and 7.45 per cent of aluminum and found that silver has a marked effect in improving the tensile strength of the magnesium alloys containing aluminum at temperatures up to 200 °C. Alloys of this type were found to have excellent properties in the heat-treated condition. An alloy of the following nominal composition: 8 per cent aluminum, 2.5 per cent silver, 0.4 per cent manganese, 0.2 per cent calcium, and the remainder magnesium, was prepared, forged, and heat treated. The heat treatment consisted of a solution treatment at 410 °C for 2 hours, followed by precipitation treatment at 175 °C for 3 days. The tensile strength after this heat treatment was about 60,500 p.s.i. and the .1 per cent proof stress about 38,000 p.s.i., an exceptional value for magnesium-base alloys. This alloy has about two-thirds the specific gravity of duralumin, and has about the same order of tensile and yield strength.

An alloy of nominal composition, 2.6 per cent aluminum, 0.2 per cent manganese, 2.6 per cent zinc, 5.5 per cent silver, and the remainder magnesium<sup>8</sup> has a specific gravity of 1.89 (0.068 lb. per cu. in.), approximate

coefficient of thermal expansion of 0.000016 per degree Fahrenheit, and after suitable heat treatment shows the following typical properties:

Table 23.—Typical Properties of Magnesium-Aluminum-Zinc-Silver Alloy  
(Heat-treated and Aged for Best Properties).

	Tensile Strength (lb/sq in.)	Yield Strength (lb/sq in.)	% Elong.	Brinell Hardness
Extruded bars up to 1½" dia.	55-65,000	40-50,000	6-8	90-95
Extruded bars (5" dia.)	50-55,000	35-45,000	3-6	85-90
Structural sections up to 3" channel	55-60,000	40-45,000	5-10	90-95
Forgings (large)	40-50,000	32-40,000	2-6	80-85

The alloy described has a resistance to corrosion that is comparable to that of all but the most corrosion-resistant commercial magnesium alloys.

Work undertaken by the Project on complex alloys of magnesium containing silver is discussed in Chapter 4.

Guertler<sup>9</sup> has suggested consideration of hardening silver-rich alloys by the addition of magnesium, and describes an alloy with 7 per cent of magnesium as being three times as hard as pure silver. Jordan, Grenell, and Herschman prepared sheet from alloys containing 1.4, 5, and 10 per cent magnesium. Only the 1.4 per cent magnesium alloy could be rolled to a sheet having a good surface. The alloys with higher magnesium content had a yellowish cast on their polished surface. Only the 10 per cent alloy showed greatly improved physical properties. Its value for tensile strength of 63,000 pounds per square inch with elongation of 46 per cent, and hardness of 107 Brinell are to be compared with the corresponding values for sterling silver, as reported by these same investigators, of 44,000 pounds per square inch tensile strength, 46 per cent elongation and 77 Brinell hardness. The effect of magnesium can be compared with that of other elements added to silver as shown in Figure 1. The Project has noted the effect of a small addition of magnesium to silver-rich alloys of silver and silicon. The data are given and discussed in this chapter under silicon-silver alloys.

According to U. S. Patent 1,784,640, an alloy of silver with 10 per cent magnesium is suitable for use as the head of poppet valves, because of its high hardness and thermal conductivity.

The addition of up to 1.5 per cent of silver to magnesium-rich alloys is claimed (U. S. Patent 1,941,039) to refine the grain structure of the alloy and prevent intercrystalline liquation. Paine (U. S. Patent 1,984,151) claims to have found that magnesium-base alloys containing from 0.5 to 8.0 per cent of silver not only exhibit a very satisfactory combination of strength and ductility in the wrought condition, but also are unusually resistant to corrosion in a 3 per cent aqueous solution of sodium chloride.



in each other in the solid state. Arrivant showed that up to 20 per cent of manganese was soluble in silver in the solid state, and stated that a compound  $MnAg_2$  was formed, which formed an unbroken series of solid solution alloys with silver and was insoluble in hydrochloric acid. Hansen and Sachs<sup>3</sup> confirmed the existence of the solid solution region, shown in the diagram, by electrical resistivity measurements.

### (b) Properties

Arrivant<sup>2</sup> noted the resistance of the silver-rich alloys to etching by hydrochloric acid. He found the 95-per cent manganese alloy too brittle to prepare for microscopic examination. Hansen and Sachs<sup>3</sup> found a moderate increase in hardness as manganese increased up to nearly 20 per cent, and a continuous increase in resistivity of from 4.88 microhm-cms at 1.26 per cent manganese to 36.3 microhm-cms at 16.5 per cent manganese. Siebe<sup>4</sup> studied the resistance of the silver-rich phase to various reagents, and found a sharply defined limit of attack between 74 and 76 atomic per cent of silver. The occurrence of such limits in other solid solution alloys is discussed by Tammann.<sup>5</sup>

Goetzel<sup>6</sup> prepared alloys of silver with 10, 15, and 20 per cent manganese, and found that the first two cast well, could be rolled and machined. The 20 per cent alloy, owing to lack of miscibility which he states may have been due to impurities in the manganese, was only moderately ductile and machinable. A somewhat harder alloy was obtained by adding 1.5 per cent of silicon to an 11 per cent manganese alloy, which also was machinable and ductile.

Table 24.—Physical Properties of Some Manganese-Silver Alloys.

Mn Content (%)	Vickers Number		Tensile Strength p. s. i.		Yield Strength* p. s. i.		Elongation (% in 2")		Resistivity microhm-cm (20 °C)	
	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>
2.63	32	69	22,700	31,200	6,780	30,900	41	8.0	8.6	9.1
6.62	46	85	27,300	37,700	9,800	35,900	32	4.0	18.2	19.4
16.16	86	122	41,900	58,000	20,800	55,500	23	2.5	39.7	37.9
19.82	86	127	43,600	58,400	23,300	54,300	18	2.0	43.2	39.6

<sup>1</sup> Annealed for 1 hour at 700 °C.

<sup>2</sup> Cold-rolled 30%, 15 B. & S. to 18 B. & S. gauge.

\* 0.2% offset method.

The mechanical properties of some manganese-silver alloys have been studied by Saeftel and Sachs.<sup>7</sup> Table 24 summarizes data obtained by the Project on manganese-silver alloys prepared from electrolytic manganese of high purity (99.9 per cent). The effect of 2.5 per cent manganese on the annealing properties of silver is shown in Figure 5. The effect of adding small amounts of silicon and nickel to similar alloys is shown in Table 25.

Experiments conducted by the Project gave evidence of precipitation-hardening in the alloy with 16.3 per cent of manganese, 0.2 silicon, and

Table 25.—Physical Properties of Manganese-Silver Alloys Containing Silicon and Nickel.

Containing Silicon and Nickel													
Composition (%)				Vickers Number		Tensile Strength		Yield Strength*		Elongation		Resistivity	
Mn	Si	Ni	Ag	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	p. s. i.		p. s. i.		(% in 2")		(20 °C)	
				An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>
7.65	0.90	—	Rem. <sup>3</sup>	50	83	23,200	31,900	10,250	30,800	19	2	15	18
13.60	0.36	—	Rem. <sup>3</sup>	60	102	26,550	42,900	14,500	42,450	11	2	32	35
15.97	0.43	—	Rem. <sup>3</sup>	59	106	—	45,900	—	45,150	—	2	—	42
16.29	0.20	0.81	Rem. <sup>3</sup>	74	114	37,650	49,800	23,050	48,950	23	2	43	47
17.12	0.15	—	Rem. <sup>3</sup>	60	100	33,950	47,700	15,650	47,050	29	2	44	48
19.55	0.06	—	Rem. <sup>3</sup>	83	127	46,500	55,150	22,700	53,800	20	2	48	51

<sup>1</sup> Annealed for 1 hour at 600 °C<sup>2</sup> Cold rolled 30%, 15 B. & S. to 18 B. & S. gauge.<sup>3</sup> Remainder

\* 0.2% offset method

0.8 nickel, and in the alloy with 19.5 per cent of manganese and 0.06 of silicon. The quenched specimens were cold-rolled 30 per cent and aged for 1 hour at 300 °C, and gave Vickers hardness numbers of about 125 and 140, respectively. The hardness diminished on heating to higher temperatures. The silver alloys with 6.6 per cent or more of manganese have markedly higher annealing temperatures than pure silver. These alloys lose their hardness after 1 hour's heating at a temperature of 350 to 400 °C.

It was observed in handling the high manganese alloys that they did not possess a metallic ring in the annealed state. This may be an indication of a high damping capacity. Cold-rolling partially restored the metallic ring of such specimens.

According to R. S. Dean,<sup>8</sup> some of the binary manganese-silver alloys prepared by the Project exhibited weak magnetic properties. This could not be confirmed. However, Potter<sup>9</sup> has found magnetic properties in manganese-aluminum-silver alloys. The maximum saturation intensity of about 70 units per cc occurs at or near the composition represented by 5 atoms of silver, 1 of manganese, and one of aluminum. Alloys of this type have a Curie point at about 360 °C and an enormous coercive force, which in the magnetic specimens is about 5000 gauss, but which in many cases exceeds this figure.

De Marchi has studied the resistance of manganese-silver alloys to corrosion in a 3 per cent sodium chloride solution, and reports an increase in corrosion resistance of the alloys containing from 4 to 20 per cent manganese. These alloys appear to form a protective chloride film.

The addition of manganese has been found by the Project to reduce the reflectivity of the alloy.

### (c) Applications

The use of manganese-silver alloys in electrical contacts is discussed in Chapter 12. No other commercial application of importance appears to have been developed, but the excellent physical properties and corrosion-resistance of manganese-silver alloys indicate possible applications in the chemical industry.

## (a) Constitution

## 25. Mercury-Silver

Figure 30 is the constitutional diagram for mercury-silver alloys, based on the work of Day and Mathewson<sup>1</sup> and Murphy.<sup>2</sup> Although the constitution of this system has attracted the attention of many investigators, it remained for the very careful thermal and microscopic

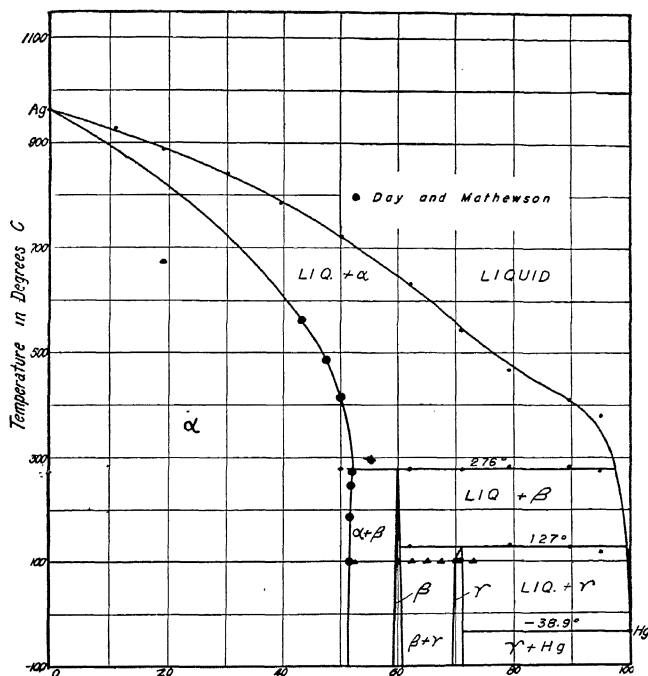


FIGURE 30. Mercury-silver constitutional diagram.

Day and Mathewson: *Trans. A.I.M.M.E.*, 128, 261 (1938).

Murphy: *J. Inst. Metals*, 40, 507 (1931).

investigation by Murphy<sup>2</sup> to give the diagram in its accepted form. The compositions of the intermediate phases were confirmed and supplemented through x-ray analyses by Preston<sup>3</sup> and Stenback.<sup>4</sup> According to Murphy, at 276 °C silver is able to dissolve 44 to 45 per cent of mercury, which may increase at lower temperatures to about 50 per cent. Preston<sup>3</sup> concluded that the saturation boundary occurred at about 46 per cent at 100 °C. Day and Mathewson,<sup>1</sup> using x-ray methods, found a solubility of 52.4 per cent of mercury in silver at 276 °C, which decreases

at lower temperature to a value of about 51.6 per cent of mercury at 100 °C.

The solubility of silver in mercury, according to Maurer,<sup>5</sup> is .065 atomic per cent at 19.2 °C, and .040 atomic per cent at 5.7 °C.

### (b) Properties

The electrical conductivity of silver amalgams has been studied by Mathiessen and Vogt,<sup>6</sup> Weber,<sup>7</sup> Batelli,<sup>8</sup> Calvo,<sup>9</sup> Parravano and Jovanovich,<sup>10</sup> and their data reviewed by Johns and Evans.<sup>11</sup>

The surface tension of silver amalgams has been studied, in the range 0 to 0.2 atomic per cent silver, by Bering and Pokrovsky.<sup>12</sup>

Gray and Bailey imply that mercury-silver alloys are tarnish-resistant, according to statements made in U. S. Patents 1,720,215 and 1,720,216, relating to the prevention of tarnish in silverware by means of a superficial alloy of this nature.

### (c) Applications

The chief interest in mercury-silver alloys is in their use in dental amalgams, as mentioned in Chapter 18. For this purpose an alloy of silver and tin is amalgamated with mercury, and has the property of "setting" to a hard mass. An explanation for this behavior is advanced by Gayler,<sup>13</sup> who suggests that the changes taking place on setting are to be attributed to complex reactions which probably do not proceed to completion. On the basis of Gayler's ternary diagram<sup>13</sup> for the Hg-Ag-Sn system, these may be summarized as:

- (1)  $\text{Ag}_3\text{Sn} + \text{Hg} \longrightarrow \text{beta}_1 + \text{gamma}_2$
- (2)  $\text{beta}_1 + \text{gamma}_2 \longrightarrow \text{beta}_1 + \text{gamma}_1 + \text{gamma}_2$

The marked contraction or expansion is attributed to the formation of a solid solution of mercury in  $\text{Ag}_3\text{Sn}$ . Troiano<sup>14</sup> disagrees with this hypothesis and offers the following alternative theory of setting, whereby the setting reaction takes place in two parts, namely:

- (1)  $\text{Ag}_3\text{Sn} + \text{Hg} \longrightarrow \text{gamma}_1 + \text{delta}_2 + \text{Ag}_3\text{Sn (unattacked)}$

This completes the reaction between solid and liquid, and terminates the actual "hardening" reaction. Subsequently the alloy should tend to approach equilibrium by the further reaction

- (2)  $\text{gamma}_1 + \text{delta}_2 + \text{Ag}_3\text{Sn (unattacked)} \longrightarrow$   
 $\text{gamma}_1 + \text{gamma}_2 \longrightarrow \text{gamma}_1 + \text{gamma}_2 + \text{beta}_1$

The expansion, Troiano proposes, may be explained by the dendritic growth of the  $\text{gamma}_1$  phase from the melt, with the consequent production of voids. Contraction may be explained by the precipitation of  $\text{delta}_2$  in the interstices of the  $\text{gamma}_1$  dendrites, which would tend to eliminate the voids.

An interesting application of mercury-silver alloys in joining copper to copper or copper to silver at temperatures below the softening point for hard-rolled copper is described by Weder in U. S. Patents 2,094,482 and 2,094,483. This process of amalgamation and diffusion alloying to effect the bond is being used in the electrical industry.

## 26. Molybdenum-Silver

### (a) Constitution

According to Dreibholz,<sup>1</sup> silver in the solid state does not dissolve any molybdenum, but in the liquid state it may dissolve at the very least about 5 per cent of molybdenum.

### (b) Properties

Molybdenum-silver alloys can be produced by sintering the powdered metals. These alloys combine the high electrical conductivity of silver and the refractory nature of molybdenum. Silver "wets" hard metal carbides and may be used as a matrix for molybdenum (or tungsten) carbide.

### (c) Applications

Molybdenum-silver alloys, with or without additions of carbon, lead oxide, etc., are used in the electrical industry for certain types of make-and-break contacts. The alloy containing 40 per cent of silver and 60 per cent of molybdenum has been used for resistance-welding electrodes for the welding of aluminum.<sup>2</sup>

## 27. Nickel-Silver

### (a) Constitution

Figure 31 is the constitutional diagram for nickel-silver alloys, based on the work of Petrenko,<sup>1</sup> Guertler and Bergmann,<sup>2</sup> and Tammann and Oelsen.<sup>3</sup> Petrenko found that two conjugate liquid phases were present at elevated temperature, except for a small solubility of silver in nickel at temperatures near the melting point of nickel, and a lower solubility of nickel in molten silver. He reported that, in the solid state, alloys containing up to 4 per cent of silver were homogeneous, but found no appreciable solubility of nickel in silver. Guertler and Bergmann<sup>2</sup> concluded that silver is rejected by the nickel-rich beta crystals as the temperature falls below the eutectic temperature, which marks the temperature of maximum solubility. Tammann and Oelsen<sup>3</sup> established the solubility of traces of nickel in silver by a magnetic method, and reported that the solubility diminished from 0.102 per cent at 922 °C to 0.012 per cent at 400 °C. For this reason, the alpha phase is indicated, although it is of too narrow limit to show on the diagram as drawn. De Cesaris<sup>4</sup> confirmed the presence of a eutectic near the nickel end of the diagram, but Petrenko's temperature for the eutectic transformation has been



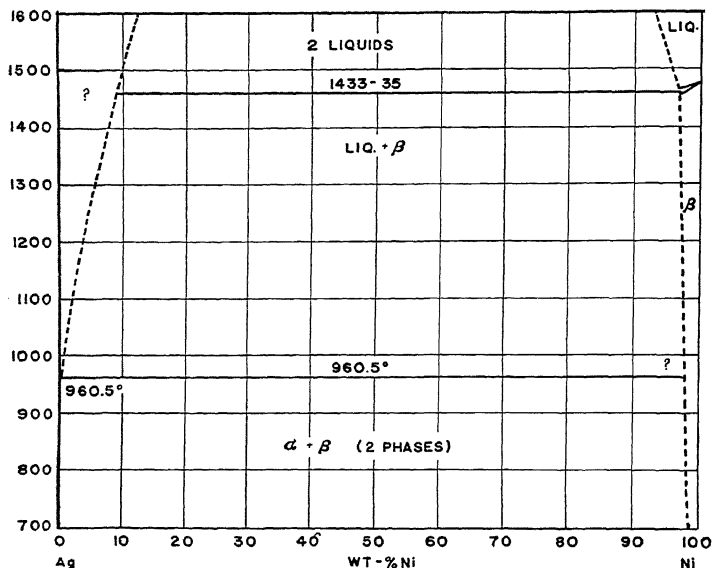


FIGURE 31. Nickel-silver constitutional diagram.

Guertler and Bergmann: *Z. Metallkunde*, 25, 53 (1933).

Tammann and Oelsen: *Z. anorg. allgem. Chem.*, 186, 264 (1930).

P. de Cesaris: *Z. Physik. Chim.*, 67, 683 (1909); *Gazz. chim. ital.*, 43, 375 (1913).

Petrenko: *Z. anorg. allgem. Chem.*, 68, 212 (1907).

revised downward in agreement with a correction necessary for the melting point of nickel reported by Petrenko (1484 °C). The temperature of the transformation, according to de Cesaris, is 1435 °C. The eutectic composition is at about 95 per cent of nickel. Vigouroux<sup>5</sup> measured the electromotive force of alloys containing from 10 to 95 per cent of silver and also made analyses of the alloys; he concluded that no compound was found, and that a small proportion of silver is soluble in nickel.

### (b) Properties

Frölich<sup>6</sup> has shown that the presence of a fractional percentage of nickel in silver tends to refine the grain and restrain grain growth on heating. The optimum effect is obtained with about 0.25 per cent of nickel. This has been confirmed by the Project. Table 26 summarizes some data obtained by the Project on the properties of nickel-silver alloys. It will be noted that a small addition of nickel increases the yield strength of annealed silver very markedly. Silver containing 0.6 per cent of nickel, given a cold reduction of 50 per cent, has an annealing temperature from 50 to 100 °C higher than that of pure silver under

comparable conditions. The effect of introducing a small proportion of silicon and heat-treating the nickel-silver alloy is discussed under silicon-silver alloys.

It may be expected that the presence of finely divided particles of nickel in the silver matrix is conducive to improved machinability. The addition of sufficient silver to nickel or nickel-rich alloys to exceed the small solubility limit should similarly impart improved machinability to such alloys.

Table 26.—Physical Properties of Nickel-Silver Alloys.

Nickel Content (%)	Vickers An- nealed <sup>1</sup>	Number Cold rolled <sup>2</sup>	Tensile Strength p. s. i.		Yield Strength* p. s. i.		Elongation (% in 2")		Resistivity microhm-cm (20 °C)	
			An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>
0.0	27	72	20,950	29,800	4,300	28,700	48	7	1.6	1.6
0.10	41	81	23,200	34,750	11,750	32,350	26	4	1.8	1.8
0.6 <sup>3</sup>	46	92 <sup>3</sup>	26,650	43,500	8,800	41,000	42	6	1.7	1.8

<sup>1</sup> Annealed for 1 hour between 700–760 °C

<sup>2</sup> Cold rolled 30% 15 B. & S. gauge to 18 B. & S. gauge.

<sup>3</sup> Sheet cold rolled 50% to 0.032" before testing.

\* 0.2% offset method.

Johnson and Mathers<sup>7</sup> have commented on the improvement in hardness of silver electrodeposits produced by the co-deposition of a fractional percentage of nickel. The effect of nickel in inhibiting grain-growth is of advantage in silver sheet fabricated by fusion welding.

### (c) Applications

An interesting commercial application of nickel-silver alloys is the use of an alloy containing about 4 per cent of silver as a master alloy for introducing silver into stainless steels. Attempts to introduce silver into such alloys directly are usually unsuccessful, whereas the use of the master alloy insures the distribution of silver in a uniformly dispersed and finely divided state.

Small additions of nickel to silver-rich contact alloys are considered beneficial and some use is made of such alloys. Other silver-rich alloys may contain a fractional percentage of nickel as a "hardener" and grain-refiner.

The possibility of using nickel-copper-silver alloys and nickel-copper-zinc-silver alloys for coinage and other purposes has been considered by Guillet, Petit, and Cournot,<sup>8</sup> Gleason,<sup>9</sup> and by Pfister and Wiest.<sup>10</sup> Some work undertaken by the Project to note the effect of adding silver to cupro-nickel alloys is discussed in Chapter 4. Pfister and Wiest's work indicates that copper alloyed with a small percentage of nickel and silver would be useful for service under continued load at elevated temperature such as is encountered by stay rods in locomotive fire-boxes.

## (a) Constitution

## 28. Palladium-Silver

Figure 32 is the constitutional diagram for palladium-silver alloys, based on the work of Ruer.<sup>1,2</sup> The two metals form a continuous series of solid solutions, as indicated. The work of other investigators substantiates the earlier work of Ruer.<sup>1</sup>

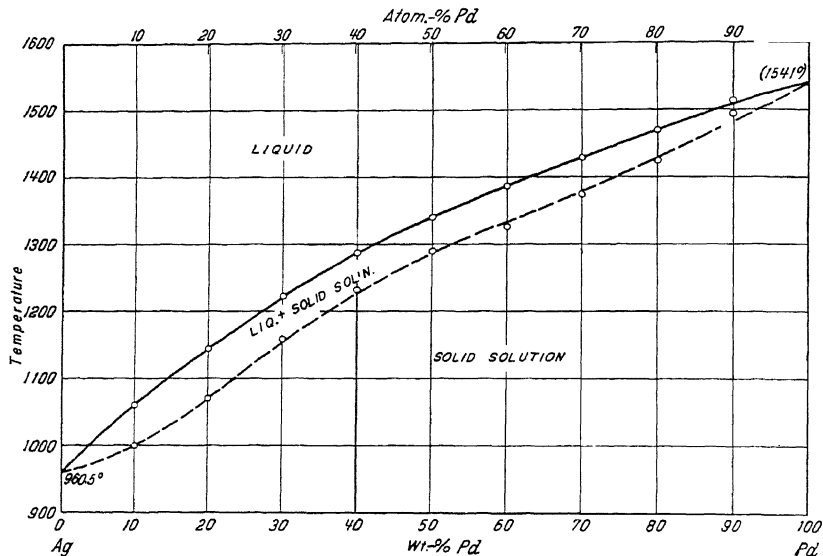


FIGURE 32. Palladium-silver constitutional diagram.

Glander: Metallwirt, 18, 337 (1939).

Ruer: Z. anorg. allgem. Chem., 51, 223, 315 (1906).

## (b) Properties

According to Wise, Crowell, and Eash,<sup>3</sup> the alloys are all soft and extremely ductile. The tensile strength of alloys annealed at 800 °C attains a maximum of 59,500 pounds per square inch at 69.8 per cent palladium. The addition of palladium to silver produces an improvement in tarnish resistance, quite marked at approximately 40 per cent palladium. The resistance to corrosion in dental work becomes satisfactory when the palladium content exceeds about 50 to 55 per cent. All the alloys are white, although those of intermediate composition are less white than the pure component metals.

Silver reduces the absorption of hydrogen by palladium, but, according to Graham,<sup>4</sup> much less than does copper. Rosenhall has investigated the palladium-hydrogen-silver alloys by x-ray and electrical resistivity

methods.<sup>5</sup> Johansson<sup>6</sup> has determined the temperature coefficient of expansion of palladium-silver alloys. According to Capillon (U. S. Patent 1,999,864) and Wise (U. S. Patent 2,129,721), the addition of a few per cent of platinum to palladium-silver alloys greatly improves their resistance to acid corrosion and tarnish. Truthe (U. S. Patent 2,143,217) asserts that a grain-refining effect is produced by the addition of a small percentage of metals like iridium, ruthenium, and rhodium.

### (c) Applications

These alloys are apparently most generally used in modified form. Copper in substantial amount may be present, as discussed by Wise in U. S. Patents 1,913,423 and 1,935,897; it imparts hardening properties. Other elements likely to be present in commercial alloys are gold and platinum. Alloys of this type find dental applications (see Chapter 18), as well as applications in electrical contacts, pen points, etc.

## 29. Phosphorus-Silver

### (a) Constitution

Figure 33 is the constitutional diagram for phosphorus-silver alloys near the silver end of the system at atmospheric pressure, as established by Moser, Fröhlich, and Raub.<sup>1</sup> Molten silver at 960 °C can dissolve 1.45 per cent of phosphorus. The eutectic composition corresponds to 2.7 per cent of  $\text{AgP}_2$  or 0.97 per cent of phosphorus. The eutectic tem-

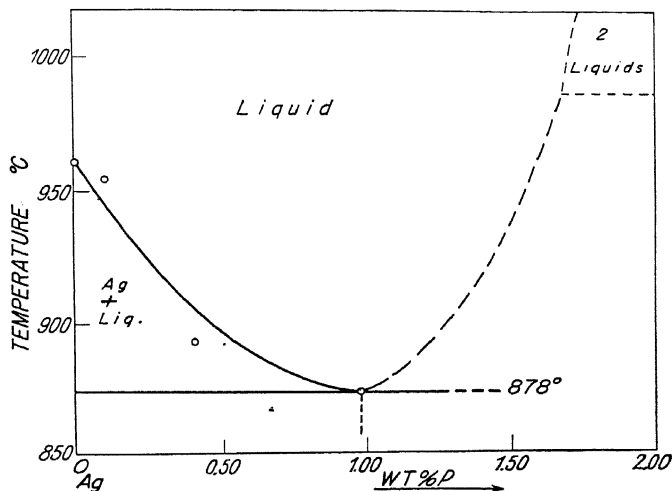


FIGURE 33. Phosphorus-silver constitutional diagram.

Moser, Fröhlich, and Raub: *Z. anorg. allgem. Chem.*, 208, 229 (1932).

perature is about 878 °C. In the hypo-eutectoid alloys the primary silver crystals are surrounded by a network of the Ag-Ag<sub>3</sub>P eutectic. The solubility of phosphorus in silver in the solid state is somewhat less than 0.026 per cent phosphorus, as an alloy of this composition reveals the presence of a low-melting eutectic even after long annealing. Haraldsen and Biltz<sup>2</sup> studied this system at higher pressures and identified the compounds Ag<sub>3</sub>P<sub>2</sub> (36.51 per cent phosphorus) and AgP<sub>3</sub> (46.32 per cent phosphorus).

### (b) Properties

It is to be expected from the microstructure of silver-phosphorus alloys that the ductility of the alloy is reduced by the presence of the less ductile phosphide intercrystalline network, and that the hot-working temperature must not exceed the melting point of the phosphide eutectic. The real interest in the phosphorus-silver system is its relation to the properties of copper-silver alloys which have been treated with phosphorus as a deoxidizer. In the absence of any deoxidizer, the alloy usually contains sufficient oxygen, as copper oxide, to reduce the workability of the alloy and make it susceptible to embrittlement by reaction of the oxide with hydrogen. The surface finish obtainable on a sheet of sterling, for example, may depend on the deoxidation practice followed. Moser, Frölich, and Raub<sup>3</sup> showed that, in proper proportions, phosphorus improved the tensile strength, workability, and corrosion resistance of copper-silver alloys. Usually from 0.2 to 0.5 per cent of phosphorus is a satisfactory addition to the melt, but care must be taken to keep the melt from contact with air and allow sufficient time (1 to 2 minutes under a charcoal cover) for deoxidation. Alloys containing too much phosphorus may develop a coarse grain structure on heating.

A ternary eutectic<sup>3</sup> melting at 646 °C, composed of 17.9 per cent silver, 30.4 per cent copper, and 51.7 per cent Cu<sub>3</sub>P (7.2 per cent phosphorus) makes possible the use of certain copper-phosphorus-silver alloys for low-temperature brazing. According to Folgner,<sup>4</sup> one of the most widely used brazing alloys of this type contains 80 per cent copper, 15 per cent silver, and 5 per cent phosphorus, melts at 640 °C (1185 °F) and is free-flowing at 704 °C (1300 °F).

Moser, Frölich, and Raub<sup>5</sup> discuss difficulties encountered in attempting to silver-plate copper-base alloys containing phosphorus and recommend a brief preliminary treatment in boiling 10-per cent potassium cyanide solution to remove the Cu<sub>3</sub>P.

### (c) Applications

Alloys containing substantial proportions of silver and phosphorus are in wide use for low-temperature brazing. Such alloys are discussed at greater length in Chapter 7. Phosphorus is often employed in the form of a phosphor-copper master alloy, for deoxidation of silver-rich alloys such as sterling and coin silver.

### (a) Constitution 30. Platinum-Silver

Figure 34 is the constitutional diagram for platinum-silver alloys, based on the work of Doerinkel,<sup>1</sup> and Johansson and Linde.<sup>2</sup> The system consists of two series of solid solutions which coexist over the range 54.7 per cent of platinum to 88 per cent of platinum at the solidus temperature. The widening of the heterogeneous range at lower temperatures has been established by Johansson and Linde,<sup>2</sup> who suggest that at temperatures below 750 °C a phase approximating Pt-Ag may be formed,

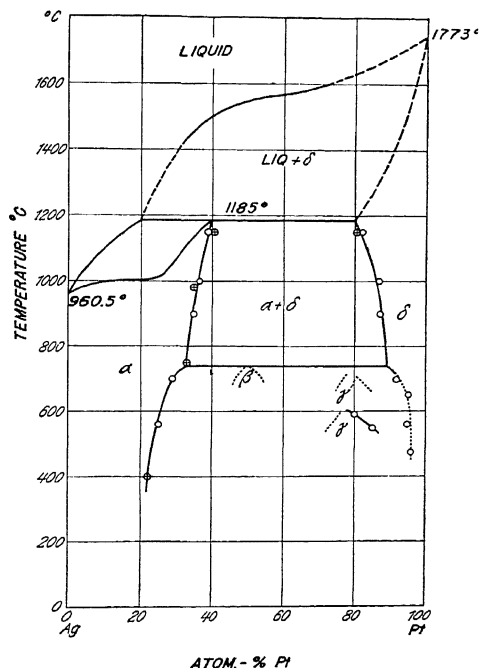


FIGURE 34. Platinum-silver constitutional diagram.

Johansson and Linde: *Ann. Phys.*, **6**, 458 (1930).

Doerinkel: *Z. anorg. allgem. Chem.*, **54**, 338 (1907).

while a second phase containing about 80 atomic per cent platinum may also be formed. The latter suffers further transformation at lower temperatures. The mutual solid solubility of the two metals decreases as the temperature falls, and affords some possibilities for precipitation hardening, particularly if some copper is also present.

### (b) Properties

According to Wise, Crowell and Eash,<sup>3</sup> melting and casting these alloys is difficult because of the propensity of silver to absorb oxygen, and of the spread between the liquidus and the solidus. Alloys containing up to 54.7 per cent of platinum may be rolled without undue difficulty, but the alloys containing between 55 and 88 per cent of platinum are extremely difficult to work, and require quenching from about 800 °C to make them even reasonably workable. The corrosion and tarnish resistance of the silver-rich alloys increase with the platinum content. The colors of the alloys are substantially white throughout, although they are less brilliant than those of the component metals.

Kurnakow and Nemilow<sup>4</sup> have determined the Brinell hardness of the binary alloys after annealing at 650 °C, and at about 1000 °C. The hardness of the alloys annealed at the higher temperature is somewhat less than for those annealed at 650 °C. The maximum hardness, about 220 Brinell, was obtained at about 75 atomic per cent platinum.

Oppitz<sup>5</sup> studied the optical constants of platinum-silver alloys (and other alloys) and found that the reflecting power of a metal of relatively low power is generally improved by mixing this metal with one of relatively higher power.

### (c) Applications

The binary alloys of platinum and silver find little use as such, but these alloys containing other elements, such as copper and gold which impart marked precipitation-hardening properties, find extensive use as dental wires and appliances. The use of silver alloys in dentistry is discussed in Chapter 18, and typical analyses of some alloys are given there. Some use is also being made of alloys of this general nature in electrical contacts.

## 31. Polonium-Silver

### (a) Constitution

Unknown.

### (b) Properties

Silver has been used, according to Whitaker, Bjorksted, and Mitchell,<sup>1</sup> as a suitable surface upon which polonium can be deposited from a solution. This has been done where an effort was being made to obtain a polonium source from old radium emanation tubes. They describe an improved method for recovering the polonium by using a rotating silver disc.

Tammann<sup>2</sup> added polonium to melts of various metals, including silver, and utilized the radioactive properties of polonium to produce a photographic record of its distribution in the alloy. In the case of silver, the concentration of the polonium in the last portions to solidify gave a beautiful picture of the silver dendrites.

## (c) Applications

Apparently silver has found use in the recovery of polonium from old radium emanation tubes. It would be interesting to follow Tammann's method in a study of crystallization in other alloys.

## (a) Constitution 32. Praseodymium-Silver

Figure 35 is the constitutional diagram for praseodymium-silver alloys, according to Canneri,<sup>1</sup> who reports the presence of three compounds:  $\text{PrAg}_3$ ,  $\text{PrAg}$ , and  $\text{PrAg}_2$ . The last compound decomposes below its melting point.

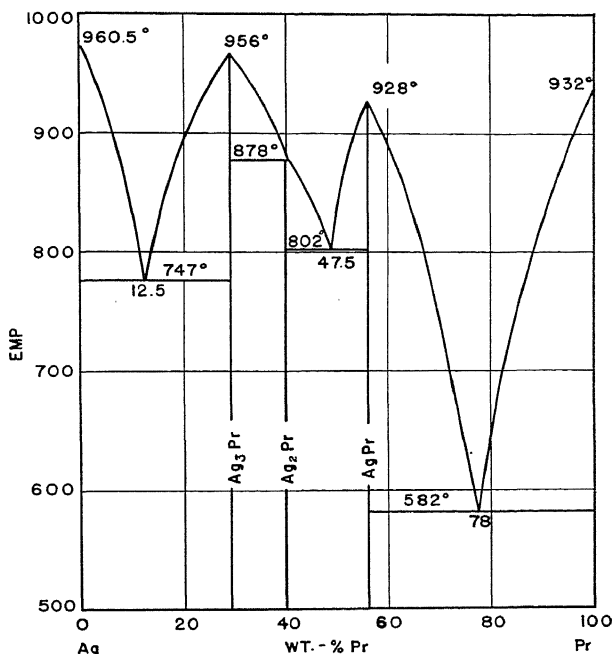


FIGURE 35. Praseodymium-silver constitutional diagram.  
Canneri: Metallurgia Italia, 26, 794 (1934).

## (b) Properties

According to Canneri,<sup>1</sup> the alloys of this system are characterized by great hardness and brittleness.

## (c) Applications

No application of alloys of this class is known.



**(a) Constitution****33. Rhodium-Silver**

According to Rössler,<sup>1</sup> rhodium is not soluble in molten silver. Drier and Walker<sup>2</sup> made an x-ray examination of alloys prepared from these metals and found them to consist of only two phases, namely, substantially pure silver and rhodium crystals containing in solid solution less than 0.1 atomic per cent of silver.

**(b) Properties**

Because of the substantially complete insolubility of these two metals, no properties of special interest occur, other than the possibility of a grain-refining effect which traces of rhodium might have on silver.

**(c) Applications**

Because of its whiteness and resistance to tarnish, rhodium is being used as a protective electroplate on silverware.<sup>3, 4</sup> Rhodium-plated ware is non-tarnishing, but the color is not quite equal to that of silver. Although rhodium has a high optical reflectivity (78-82 in the visible range) it is inferior to silver in this respect.

**(a) Constitution****34. Selenium-Silver**

The constitution of selenium-silver alloys has been studied by Pellini,<sup>1</sup> Roessler,<sup>2</sup> Friedrich and Leroux,<sup>3</sup> and Pélabon.<sup>4</sup> Hansen<sup>5</sup> has summarized their results in a constitutional diagram.

A compound,  $\text{Ag}_2\text{Se}$ , occurs at 26.8 per cent selenium. The compound exists in the beta form above 122 °C. Considering the Ag- $\text{Ag}_2\text{Se}$  system, the addition of selenium to silver lowers the freezing point to about 890 °C at 9 per cent selenium. An isothermal transition occurs at this temperature, two liquid phases appearing of composition 9 per cent selenium and about 25 per cent selenium. The eutectic occurs at about 26 per cent selenium between 834 and 850 °C. Apparently the eutectic consists of pure silver and the compound beta- $\text{Ag}_2\text{Se}$ . In the  $\text{Ag}_2\text{Se}$ -Se system, the liquidus falls from 897 °C at 26.8 per cent to about 616 °C at 37 per cent selenium, where a second liquid phase appears, quite rich in selenium. Solidification is complete at 217 °C and the two solid phases are beta- $\text{Ag}_2\text{Se}$  and Se. The transition of the  $\text{Ag}_2\text{Se}$  from the beta form to alpha- $\text{Ag}_2\text{Se}$  occurs at about 122 °C.

**(b) Properties**

The unusual electrical characteristics of the silver-selenide, and the related sulfur and tellurium compounds, have been discussed by Tubandt, Reinhold, and Neumann.<sup>6</sup> The selenide is a semi-conductor possessing electrolytic conductivity.

**(c) Applications**

No application is known to the author.

## (a) Constitution

## 35. Silicon-Silver

Figure 36 is the constitutional diagram for silicon-silver alloys based on the work of Arrivant,<sup>1</sup> Corson,<sup>2</sup> and the Project staff. Arrivant<sup>1</sup> determined the liquidus and solidus curves for the system and found a solubility of about 10 per cent of silver in silicon at the eutectic temperature. His lowest silicon alloy was 2 per cent silicon, and he did not detect any solubility of silicon in silver. The eutectic was located at about 4.5 per cent of silicon. Corson<sup>2</sup> located the eutectic at nearly 4 per cent of silicon, and states that a small proportion of silicon, probably not exceeding 0.2 per cent, is soluble in silver at higher temperatures,

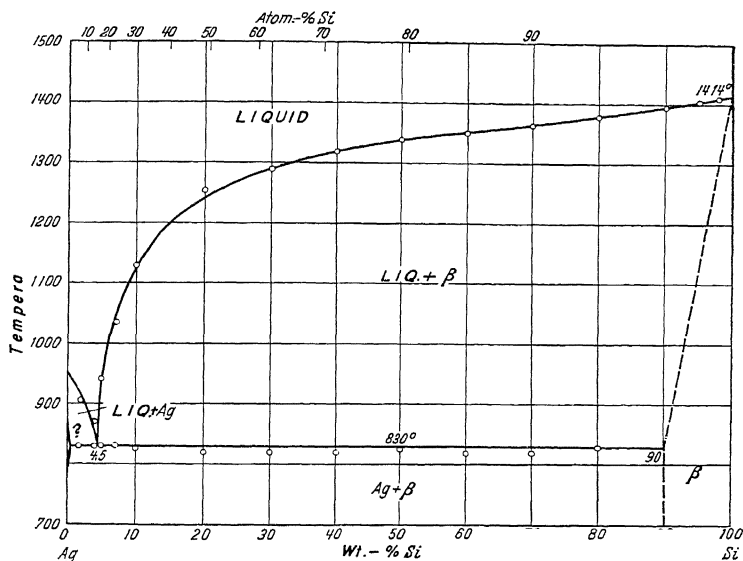


FIGURE 36. Silicon-silver constitutional diagram (Silver Research Project).

Corson: Iron Age, 119, 421 (1927).

Arrivant: Compt. rend., 147, 859 (1908).

but precipitates on annealing at lower temperatures. As a consequence, low-silicon alloys show precipitation-hardening. The Project confirmed this behavior in the case of low-silicon alloys, although the limit of solubility was not determined. Jette and Gebert<sup>3</sup> state that the solid solubility of silver in silicon is on the order of 0.2 per cent.

## (b) Properties

According to Corson<sup>2</sup> the alloys containing up to 4 per cent of silicon may be hot- and cold-worked, and the eutectic alloy is remarkably

resistant to tarnishing. An addition of cadmium, tin or zinc permits bringing the alloy to sterling composition and, he suggested, this procedure would open a way to the manufacture of tarnish-resisting silver articles. He noted the tendency of silver crystals to segregate and interfere with the polishing quality of the alloy. According to Corson an alloy of silver with 0.2 per cent of silicon could be heat-treated to increase the hardness from 55 to 70 Brinell (500 kg/10 mm), and the hardening effect could be substantially increased by having sufficient copper present to form  $\text{Cu}_3\text{Si}$  (1.5 per cent copper). He produced such an alloy containing over 98 per cent silver which, in the wrought condition, quenched from 800 °C and aged at 200 °C, exhibited an increase in strength and a Brinell hardness of 100.

Ray and Baker<sup>4</sup> observed that silicon had a marked hardening effect on silver alloys, but failed to find any marked effect on tarnish resistance. The Project has confirmed these conclusions, but, unlike Ray and Baker, found it possible to work alloys containing up to 4.4 per cent of silicon.

Table 27.—Physical Properties of Binary Silicon-Silver Alloys.

Silicon Content (%)	Vickers	Number	Tensile Strength		Yield Strength*		Elongation		Resistivity	
			p. s. i.		p. s. i.		(% in 2")		microhm-cm (20 °C)	
	Annealed <sup>1</sup>	Cold-rolled <sup>2</sup>	Annealed <sup>1</sup>	Cold-rolled <sup>2</sup>	Annealed <sup>1</sup>	Cold-rolled <sup>2</sup>	Annealed <sup>1</sup>	Cold-rolled <sup>2</sup>	Annealed <sup>1</sup>	Cold-rolled <sup>2</sup>
0.0	27	72	20,950	29,800	4,300	28,700	48	7	1.6	1.6
0.31	35	88	24,450	37,700	11,700	35,900	45	6	—	4.0
0.87	43	95	27,650	41,550	10,650	39,750	36	5	3.8	4.0
1.63	54	104	31,600	45,750	13,400	43,750	32	4	4.3	4.3
4.43	63	111	28,650	46,900	14,900	46,400	12	2	5.0	5.4

<sup>1</sup> Annealed 1 hour at 700 °C

<sup>2</sup> Cold Rolled 30%, 15 B. & S. to 18 B. & S. gauge.

\* 0.2% offset method.

Table 27 summarizes some data obtained by the Project on a group of binary silicon-silver alloys. It will be noted that as little as 0.3 per cent of silicon very greatly improves the yield strength of silver in the annealed condition. The effect of 2.5 per cent of silicon on the annealing properties of silver is shown by curve 4 of Figure 5. Data obtained for alloys containing 0.25, 0.75 and 2.5 per cent of silicon, cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge and then annealed for one hour, showed that a silicon content of 0.25 or of 0.75 per cent raised the annealing temperature almost 100 °C, but that 2.5 per cent of silicon was less effective in this respect.

The response to heat treatment of a 1.6-per cent silicon-silver alloy rod, 0.25 inch in diameter, is shown in Figure 37. Curve 4 is from data obtained by the Project, the other curves represent data supplied by Handy & Harman.<sup>5, 6</sup> The tensile strength of this alloy, in pounds per square inch, hard-rolled, was 49,100; annealed 31,200; under the conditions of curve 1, it was 41,900; of curve 2, 41,800; and of curve 3, 37,500.

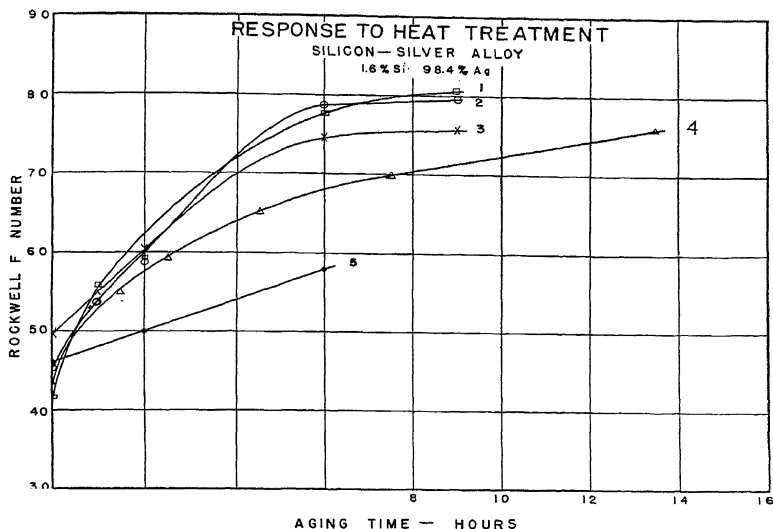


FIGURE 37. Response of 1.6% silicon-silver alloy to heat treatment.

1. 4 hours at 1420 °F, quenched in water, aged at 500 °F.
2. 2 hours at 1420 °F, quenched in water, aged at 500 °F.
3. 1 hour at 1420 °F, quenched in water, aged at 500 °F.
4. 3½ hours at 1420 °F, quenched in water, aged at 482 °F.
5. ½ hour at 1420 °F, quenched in water, aged at 500 °F.

The resistivity of the rod was 2.69 microhm-centimeters as rolled, and 3.40 microhm-centimeters after heat treatment. The average coefficient of expansion of the heat-treated rod, for the range 20 to 100 °C, was found to be 0.000183 per degree centigrade. The same value was obtained on the hard-rolled rod before the aging heat treatment.

Table 28.—Physical Properties of Some Special Silicon-Silver Alloys.

Ni	Composition				Vickers Number		Tensile Strength		Yield Strength*		Elongation		Resistivity	
	Si	Mg	Ag		An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>	An- nealed <sup>1</sup>	Cold- rolled <sup>2</sup>
Fine silver	—	—	—	Rem.*	27	72	20,950	29,800	4,300	28,700	48	7	1.6	1.6
0.07	0.87	—	Rem.*		43	90	25,850	40,700	10,500	38,500	36	3	2.6	2.6
0.05	0.79	1.19	Rem.*		46	94	26,250	40,000	11,350	37,450	27		5.2	5.5

<sup>1</sup> Annealed for 1 hour at 600 °C.

<sup>2</sup> Cold-rolled 30%, 15 B. & S. to 18 B. & S. gauge.

\* Remainder.

\* 0.2% offset method.

The Project carried out a few exploratory tests to note whether a greater hardness and strength could be obtained by precipitating a silicide than by precipitating silicon. Table 28 summarizes some of the data obtained on silicon-silver alloys to which nickel and magnesium additions had been made. The alloys were also solution-treated, quenched, cold-

rolled from No. 15 to No. 18 B. & S. gauge, and reheated to various temperatures for one hour. The alloys containing nickel and silicon, and magnesium and silicon increased somewhat in hardness on heating at 200 °C, thus indicating that some precipitation hardening occurred. The values attained were between 90 and 100 Vickers.

It was observed that a cold-rolled alloy containing 0.23 per cent of silicon and 0.06 per cent of nickel did not soften after six hours at 300 °C.

A 2-per cent silicon-silver alloy had a Brinell hardness (500 kg/10 mm) of 49, measured at 310° C.

The reflectivity of silicon-silver alloys decreases with increasing proportions of silicon. An alloy containing 1.5 per cent silicon had a reflectivity of 94 per cent.

Ellinger and Acken<sup>7</sup> who have studied the preparation of silicon-silver alloys for metallographic examination, have given illustrations of the structure of alloys containing 0.3 and 1.25 per cent of silicon.

De Marchi found (see Chapter 15) that the addition of silicon to silver did not materially affect its resistance to corrosion in brine.

Alloys containing as much as 1.65 per cent of silicon have been found to weld satisfactorily.

Corson (U. S. Patent 1,643,304) comments on the grain-refining effect of silicon in silicon-silver alloys. This effect has been confirmed.

### (c) Applications

The improved physical properties of silicon-silver alloys, as compared to fine silver, are obtained by the introduction of a chemically inert element. Consequently, there has been some consideration given to the use of alloys of this type in the chemical industry. For such applications the silicon content is kept below about 1.75 per cent to reduce the tendency toward segregation in ingots of commercial size.

Further exploration of modified silicon-silver alloys appears to be warranted.

## 36. Sodium-Silver

### (a) Constitution

Figure 38 is the constitutional diagram for sodium-silver alloys, based on the work of Quercigh and Bruni<sup>1</sup> and Mathewson.<sup>2</sup> Quercigh's data is in good agreement with that of Mathewson, but Mathewson could not confirm the solubility of 13 atomic per cent of sodium in solid silver reported by Quercigh. According to Mathewson, the maximum possible solubility of sodium in silver is 2.6 atomic per cent, or 0.61 weight per cent; and sodium does not dissolve any appreciable quantity of silver. Tammann<sup>3</sup> found that 0.3 per cent of silver lowers the freezing point of sodium by 0.09 °C. Mathewson<sup>2</sup> concluded that a eutectic exists at a few tenths per cent of silver at a temperature about 0.1 °C below the freezing point of sodium.

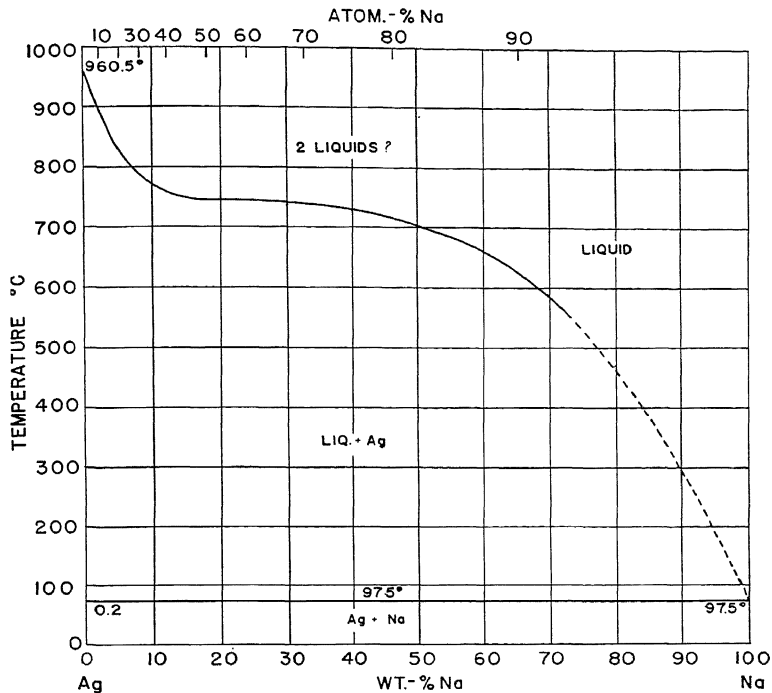


FIGURE 38. Sodium-silver constitutional diagram.

Quercigh and Bruni: *Z. anorg. allgem. Chem.*, **68**, 301 (1911).  
 Mathewson: *Int. Z. Metall.*, **1**, 51 (1911).

### (b) Properties

The alloys, *per se*, are of little interest, but the possibility of using sodium as a deoxidizer for silver-rich melts warrants consideration of this system.

### (c) Applications

Sodium, when properly used, is an effective deoxidizer for silver,

## 37. Strontium-Silver

### (a) Constitution

Figure 39 is the constitutional diagram for strontium-silver alloys based on Wiebke's data.<sup>1</sup>

## 38. Sulfur-Silver

### (a) Constitution

Figure 40 is the constitutional diagram for sulfur-silver alloys based on the work of Bissett.<sup>1</sup> This system has also been studied by Roes-

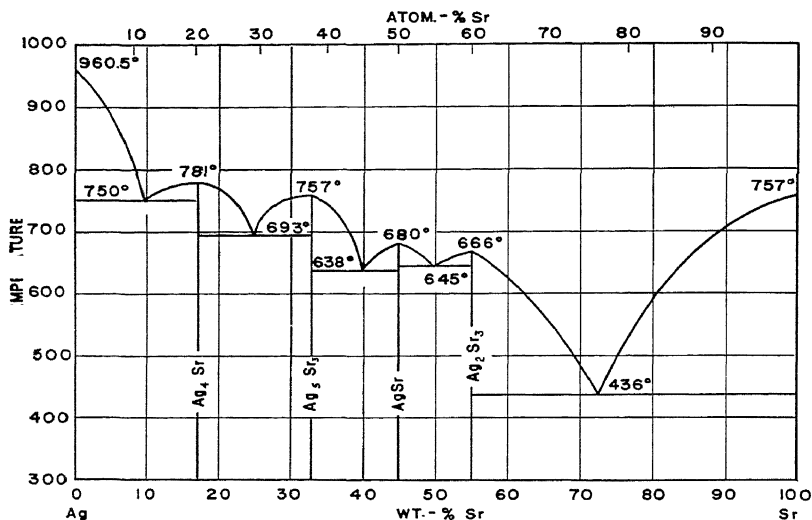


FIGURE 39. Strontium-silver constitutional diagram.

Weibke: Z. anorg. allgem. Chem., 193, 299 (1930).

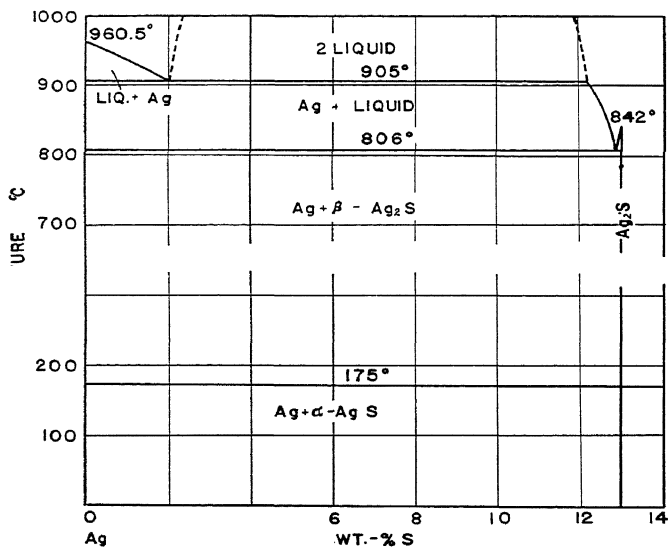


FIGURE 40. Sulfur-silver constitutional diagram.

Vrasow: Ann. Inst. Polytech. Petrograd, 23, 593 (1915).

Bissett: J. Chem. Soc., 105, 1223 (1914).

slar,<sup>2</sup> Pélabon,<sup>3</sup> Friedrich and Leroux,<sup>4</sup> Jaeger and van Klooster,<sup>5</sup> and Urasow.<sup>6</sup> The melting point of the compound  $\text{Ag}_2\text{S}$  given by Bissett (815 °C) is lower than the value (842 °C) found by Jaeger and van Klooster,<sup>5</sup> which is used on the diagram. The transformation temperature for the change from beta- to alpha- $\text{Ag}_2\text{S}$  is 175 °C. The eutectic temperature is 804-807 °C, the eutectic composition 12.8 per cent sulfur.

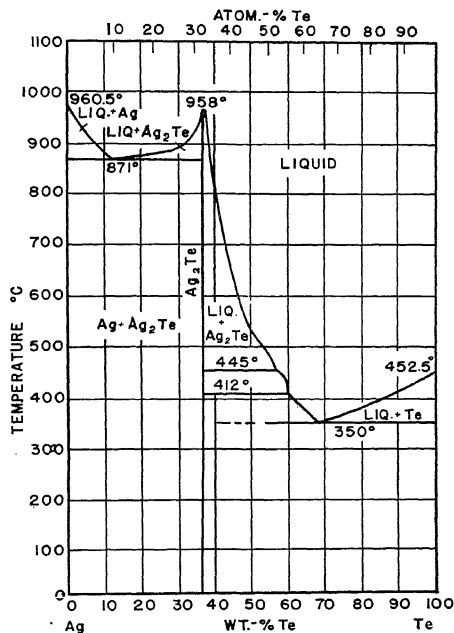


FIGURE 41. Tellurium-silver constitutional diagram.

Chikashige and Saito: Mem. Coll. Sci. Kyoto Imp. Univ., 1, 361 (1916).

### (b) Properties

Urasow<sup>6</sup> studied some properties of  $\text{Ag}_2\text{S}$  and obtained results making it possible to explain the phenomenon of the formation of silver moss from  $\text{Ag}_2\text{S}$ . He found three transformation points, namely: 576, 175, and 110 °C. The first modification forms solid solutions with up to 0.5 per cent of silver, which are unstable at lower temperature.

The tarnishing of silver in the presence of sulfur is discussed in Chapter 15, and for additional references pertaining to the system sulfur-silver, section J.2 of the bibliography should also be consulted. Some properties of silver sulfide are also discussed in Chapter 18.



### (c) Applications

Only minor applications are known, but consideration has been given by the Project to the use of silver sulfide as an ingredient in extreme pressure lubricants, as a conducting plastic for electroforming purposes, and as an addition to silver bearings.

## 39. Tellurium-Silver

### (a) Constitution

Figure 41 is the constitutional diagram for tellurium-silver alloys based primarily on the work of Chikashige and Saito.<sup>1</sup> Pébalon<sup>2</sup> and Pellini and Quercigh<sup>3</sup> also contributed to a knowledge of this system, and Hansen<sup>4</sup> has reviewed the work of these investigators. Chikashige and Saito suggested the existence of the compound  $\text{Ag}_7\text{Te}_4$  containing 59.69 per cent of silver. Apparently there exists a compound of formula either  $\text{Ag}_3\text{Te}_2$  or  $\text{AgTe}$  containing about 55 per cent of silver which undergoes a transformation at 412 °C, according to Pellini and Quercigh,<sup>3</sup> or 408-413 °C, according to Chikashige and Saito. The latter authors reported the eutectic temperatures at 870 and 351 °C, respectively. The two eutectic compositions lie between 12.5 and 16 per cent tellurium and 68 and 70 per cent.

Koern<sup>5</sup> studied this system by thermal, microscopic, and x-ray methods. His data were in general agreement with the results of Chikashige and Saito, although Koern found that only two compounds exist in the system,  $\text{Ag}_2\text{Te}$  and  $\text{Ag}_{12}\text{Te}_7$ , both of which have two modifications. The low-temperature or alpha form of  $\text{Ag}_2\text{Te}$  is orthorhombic, and alpha- $\text{Ag}_{12}\text{Te}_7$  hexagonal in structure.

### (b) Properties

Faus<sup>6</sup> has determined the temperature-electrical resistance curves for the alloys containing up to 50 per cent silver. Single crystal alloys containing 5 to 15 per cent of silver have a negative temperature coefficient of about  $-1.3$  at 25 °C and a resistivity of 1.9 to 2.8 megohms per circular mil foot at 25 °C. Properly heat-treated alloys have a practically constant temperature coefficient of resistance from  $-10$  to  $+70$  °C.

According to Skowronski<sup>7</sup> the presence of a few parts per million of tellurium in fine silver causes embrittlement.

### (c) Applications

Faus<sup>6</sup> describes the use of the 15-per cent silver alloy for temperature compensation purposes in electrical instruments.

## 40. Thallium-Silver

### (a) Constitution

Figure 42 is the constitutional diagram for thallium-silver alloys, based on Petrenko's results,<sup>1</sup> but slightly modified to take into account the more exact work of Heycock and Neville.<sup>2</sup> Petrenko placed the eutec-

tic at 97.5 per cent thallium and 287 °C, whereas Heycock and Neville placed the eutectic at 98.7 per cent thallium and 289 °C. At least 10 per cent of thallium is soluble in silver in the solid state near the eutectic temperature, according to Petrenko; but Chiswick and Hultgren<sup>3</sup> place the solubility at 287 °C at 9 per cent thallium.

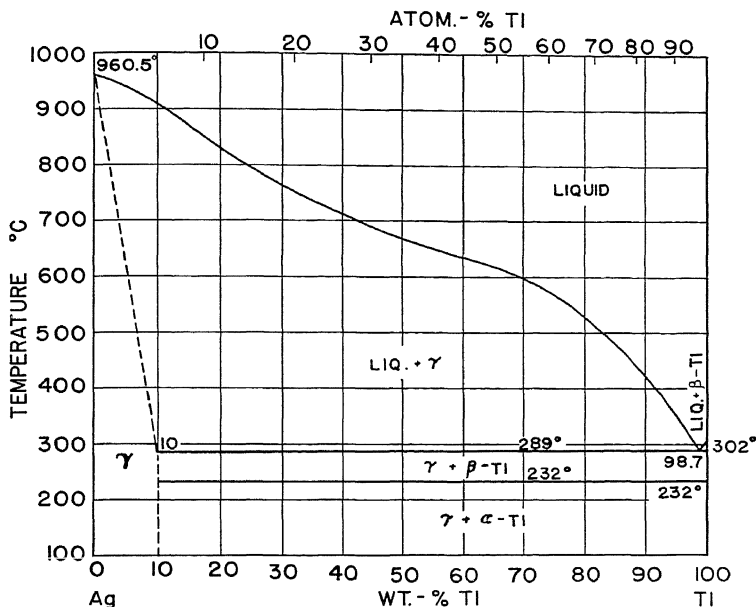


FIGURE 42. Thallium-silver constitutional diagram.

Petrenko: *Z. anorg. allgem. Chem.*, 50, 133 (1906).

Heycock and Neville: *Phil. Trans. Roy. Soc.*, 189, 55 (1897).

### (b) Properties

Hardebeck<sup>4</sup> measured the thermal conductivity of alloys containing 2.73 and 4.76 per cent thallium, and found their conductivity to be much lower than that of silver. The superconductivity of a 3-per cent silver alloy has been investigated by de Haas, Aubel and Voogt;<sup>5</sup> while pure thallium becomes superconductive at 2.37 °K, the thallium-silver alloy becomes a superconductor at 2.67 °K.

Alloys of thallium and silver<sup>6</sup> have been found to have a high luster and remain untarnished on exposure to air, and silver alloyed with aluminum and thallium is said to be extremely resistant to chemical reagents, including hydrochloric acid and hydrogen sulfide. The most satisfactory of the latter alloys contains 10 per cent of thallium, 10 per cent of aluminum, and 80 per cent of silver.

## (c) Applications

Some use appears to be made abroad of the thallium-aluminum-silver alloys, as described in U. S. Patent 1,863,612. According to U. S. Patent 1,899,465 an aluminum alloy containing from 0.2 to 1.0 per cent of silver and 0.02 to 0.2 per cent of thallium has useful properties. While this is probably not employed commercially, it is interesting to compare such an alloy with the recently studied magnesium-thallium-silver alloys<sup>7</sup>.

## 41. Thorium-Silver

Tanimmann<sup>1</sup> observed that thorium B, the lead isotope, when added to molten silver, segregated at the grain boundaries. (See also Polonium-Silver.)

## 42. Tin-Silver

## (a) Constitution

A comprehensive study of the constitution of the tin-silver alloys has been made by Murphy,<sup>1</sup> who used thermal analysis, microscopic examination, and electrical resistance methods. Murphy reported a new phase lying in the region between 12.5 and 19 per cent of tin at room temperature, with somewhat wider boundaries at high temperatures, which had escaped the attention of Petrenko.<sup>2</sup> Its existence has been confirmed by the x-ray investigations of Nial, Almin, and Westgren.<sup>3</sup>

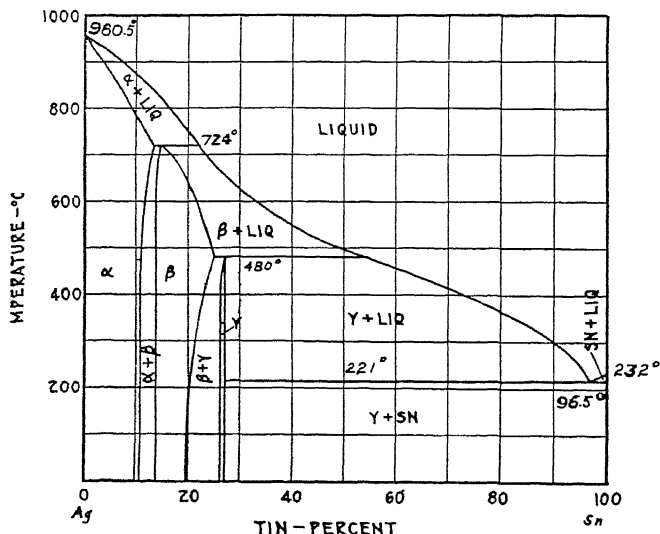


FIGURE 43. Tin-silver constitutional diagram.

Murphy: J. Inst. Metals. 35. 107 (1926).

Murphy estimated the solid solubility of silver in tin to be less than 0.1 per cent, which is in general agreement with the change of properties found for tin containing 0.02 per cent of silver by Hanson, Sandford, and Stevens,<sup>4</sup> who report a solubility of 0.07 per cent of silver in tin at 210 °C, and 0.02 per cent at 100 °C. Jenckel and Roth<sup>5</sup> found that their resistivity studies indicated a solubility of 0.1 to 0.2 per cent of silver between 40 and 200 °C. Murphy's diagram is given in Figure 43.

### (b) Properties

The observation made by Murphy that the presence of silver greatly retards the allotropic transformation from white to gray tin at low temperatures is noteworthy. Tin of 99.99 per cent purity, when maintained at -78 °C, began to change to the gray state in 6 days when in the worked condition, and in 11 days when cast material was used. However, cast tin containing 0.2 per cent or more of silver maintained at the same low temperature for 3 weeks showed no evidence of change. The same sample, removed from its low-temperature surroundings and subjected to cold-work, showed no effect after an additional period of 3 weeks at -78 °C. Inoculation of the argentiferous tin with gray tin also failed to produce any effect in 6 weeks.

According to Ireland,<sup>6</sup> alloys containing 2.5 to 5.0 per cent of silver are suitable for valves for refrigeration equipment and similar apparatus. Material of this composition is more resistant to cold plastic flow than is pure tin, but is sufficiently soft to allow hard objects to be pressed into it when desired.

Hanson, Sandford, and Stevens<sup>4</sup> demonstrated that the grain size of tin was noticeably decreased as silver was added up to 0.1 per cent and that tin containing 0.2 per cent of silver has the very high tensile strength, as compared with pure tin, of 7,500 pounds per square inch after quenching from 210 °C. However, the increase in strength over that of tin largely disappeared after 22 weeks at room temperature. On the other hand, the tin-silver eutectic alloy (3.5 per cent of silver) had maintained its high strength better, as is shown in Table 29.

Table 29.—Ultimate Tensile Strength of the Eutectic Tin-Silver Alloy.<sup>4</sup>

Condition	Ultimate tensile strength (lb/in. <sup>2</sup> )
15 days after rolling	8,100
Annealed for 3 hours at 100 °C	7,800
Annealed for 3 hours at 210 °C	5,200
Quenched from 210 °C	8,300

The results of some experiments at the National Bureau of Standards<sup>7</sup> on tin-silver alloys containing up to about 10 per cent of silver are given in Table 30. The specimens, about 0.040 inch thick, which had been rolled from ingots approximately 0.5 inch thick, were tested about 14 days after rolling.

Table 30.—Tensile Properties of Some Tin-Silver Alloys.<sup>7</sup>

Nominal silver content (%)	Actual silver content average of top and bottom (%)	Yield point <sup>1</sup> (lb/in. <sup>2</sup> )	Ultimate tensile strength (lb/in. <sup>2</sup> )	Elongation in 2 in. (%)
1.0	0.98	2,350	3,000	57
2.0	1.86	3,900	4,500	47
3.5	3.65	4,500	5,300	37
6.0	5.64	3,650	4,650	49
10.0	9.87	3,600	4,850	40
(99.99 Sn)	—	—	2,200	68

<sup>1</sup> Divider method.

The tensile strength was considerably lower than the value reported by Hanson, Sandford, and Stevens.<sup>4</sup> The alloy of approximately eutectic composition possessed the greatest strength but also the lowest elongation. Tests were also made<sup>7</sup> on the bursting strength of silver-tin pipe which had been extruded through the die used for the size known as  $\frac{3}{8}$  in. 5-oz. tin pipe. Water pressure was used and the test completed in about one minute. The following comparative values of the strength of the ordinary tin and the silver-tin pipes were obtained:

Table 31.—Comparison of Strength of Tin and Tin-Silver Pipe.<sup>7</sup>

Material	Pressure (lb/in. <sup>2</sup> )	
	Ballooning begins	Leaking begins
Tin pipe	1,300	1,700
Silver-tin pipe	2,300	2,550

The physical properties of Straits tin and an alloy containing 3.16 per cent of silver were studied by the Project. Table 32 summarizes

Table 32.—Physical Properties of Tin and Tin-3.16 Per Cent Silver Alloy.

	Vickers Number		Tensile Strength		Yield Strength*		Elongation		Resistivity microhm-cm	
	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>
Pure Tin (Straits)	7.2	8.4	2,190	2,850	1,340	1,980	45	35	11.6	11.4
Tin+3.16% Silver	11.5	14.7	3,930	5,200	1,700	3,770	50	36	11.4	11.3

<sup>1</sup> Annealed for 1 hour between 175–200 °C.<sup>2</sup> \* Cold-rolled 30% from 15 B. & S. to 18 B. & S. gauge.

\* 0.2% offset method.

the physical properties of sheet material in the annealed and 30-per cent cold-rolled condition. The cold-rolled tin-silver alloy maintained its hardness well after heating for an hour at 60 °C, but softened after one hour at 100 °C. Nevertheless, even after heating for an hour at 200 °C, it had a Vickers hardness of 12 as compared with about 7 for pure tin.

The resistance of tin-silver alloys to corrosion and abrasion has been studied by Rogers and Schoonover.<sup>8</sup> In comparative tests in boiling phenol, the tin-silver alloy containing 3.5 per cent of silver was slightly

less corroded than pure tin, but was not resistant enough for use in the production of high-purity phenol. The corrosive action of milk, 1-per cent lactic acid, and 1-per cent sodium hydroxide was noted on both tin and the eutectic tin-silver alloy. The samples were scoured, a standard cleaning procedure being used, and weight loss was determined. It was concluded that the alloy was superior to pure tin as a material for plating milk cans, primarily because of its greater ability to withstand scrubbing with alkali. The wear of the eutectic alloy in simple abrasion was found to be only six-tenths that of tin. Samples of tin and the eutectic (3.5 per cent silver) alloy were also exposed to corrosion by distilled water in a storage tank at the Bureau of Standards. After four and a half years of exposure, no significant difference in corrosion of the two materials was ascertainable; neither showed appreciable loss in weight. The author has observed that a sample of tubing of the eutectic composition had a whiter color than pure tin, and retained its brightness in a laboratory atmosphere over a period of years better than did an adjacent sample of pure tin tubing. So far as can be judged from the available data, the tin-silver alloy equals, if it does not excel, pure tin in resistance to corrosion.

The soldering characteristics of tin containing 3.5 per cent of silver have been noted by the Project. This alloy has excellent fluidity and wetting characteristics. It melts at 221 °C and handles very much like ordinary 50-50 lead-tin solder. Barham<sup>9</sup> states that tin-silver alloys containing up to 10 per cent of silver form very useful solders. The alloy containing 10 per cent of silver is completely molten at 300 °C and has a tensile strength, at room temperature, of 9000 pounds per square inch, with excellent ductility. It readily solders all the common metals (except aluminum) and works well with the ordinary fluxes. It is free-flowing and more resistant to corrosion than are lead-tin alloys, and also has a higher electrical conductivity (compare U. S. Patent 1,565,115).

Hanson and Sandford<sup>10</sup> showed that the addition of 3.5 per cent of silver to tin produced an alloy which had considerable resistance to creep, and withstood a stress four times as great as did pure tin for the same duration. Hanson and Sandford<sup>11</sup> subsequently found that alloys containing 1 or 2 per cent of silver were but little inferior in this respect to the 3.5-per cent silver alloy; they state that the working stress should not exceed 600 pounds per square inch for these alloys, and 150 pounds per square inch for pure tin. An alloy containing 1 per cent of cadmium and 3.5 per cent of silver had a remarkably high resistance to creep.

The tin-silver alloys of intermediate composition are of interest, since the usual dental alloy for the production of amalgams has a minimum content of 65 per cent silver and 25 per cent tin. The properties and uses of such alloys in dental practice are reviewed by Thompson and Wild<sup>12</sup> and are discussed in Chapter 18.

John and Evans<sup>13</sup> have determined some physical properties of the entire tin-silver system of alloys. The electrical resistivities vary but

little from that of pure tin until the composition reaches 74 per cent silver, where a marked increase occurs, reaching a maximum of about 75 microhm-cm at 0 °C, and then dropping sharply with further increase in silver. These investigators also determined the Hall coefficient, thermo-electric power with reference to copper, temperature coefficient of resistance, and densities for the entire range of composition. Allen<sup>14</sup> investigated the phenomenon of superconductivity in alloys of tin and silver. Effect of additions of tin upon some properties of silver have been investigated by Saeftel and Sachs,<sup>15</sup> who found that the hardness increased with increase of tin in a moderate manner until more than 10 per cent of tin was present, and then increased greatly as tin increased, up to nearly 16 per cent. Hansen and Sachs<sup>16</sup> and Schmidt<sup>17</sup> have determined the electrical conductivity of the silver-rich alloys.

According to Ellis (U. S. Patent 2,154,068) an alloy containing 5 per cent of tin and 95 per cent of silver has a resistivity of 20 microhm-cm, a tensile strength of 39,000 pounds per square inch in the annealed condition, and 74,000 pounds per square inch in the hard-drawn condition, and also has good properties as an electrical contact. According to Leach (U. S. Patent 1,952,082) the addition of from 6 to 7.1 per cent of tin to silver produces an alloy of sterling fineness and improved tarnish resistance.

### (c) Applications

Alloys of tin with from 3 to 10 per cent of silver are being used for solders requiring greater corrosion-resistance, or absence of toxic (lead) constituents, or a higher melting point than is possible with lead-tin solders. An alloy of approximately the eutectic composition is used for cast cock bodies, which are equipped with a fine silver plug, and are being used on distilled water lines. Alloys containing about 25 per cent of tin are used in the manufacture of dental amalgam alloys. Silver-rich alloys containing tin are used for electrical contacts, and tin is an important addition in certain hardenable high silver dental alloys. A wider application of the low-silver alloys may be expected, in view of the many applications where, although the corrosion resistance of tin is adequate, a physically superior metal is desired. Silver is the only metal capable of producing the physical improvement without objection from the standpoint of contamination or toxicity.

## 43. Titanium-Silver

### (a) Constitution

According to Hobson,<sup>1</sup> silver does not alloy with titanium. However, Rossi (U. S. Patent 1,025,426 and 1,024,476) describes a method for producing "a binary alloy of titanium with silver."

### (b) Properties

Rossi states (U. S. Patent 1,025,426) that his alloy of titanium and silver is of utility for the purpose of purifying silver.

#### (a) Constitution

### 44. Tungsten-Silver

According to Bernoulli<sup>1</sup> and Hobson,<sup>2</sup> these two metals are practically insoluble in the liquid state and insoluble in the solid state.

#### (b) Properties

By sintering a compressed mixture of the metal powders, tungsten and silver aggregates can be produced in useful form. However, it is more expedient to use a mixture of tungsten carbide and silver, to obtain the advantage of the extreme hardness of the metal carbide and retain a matrix having the electrical conductivity and other properties of silver. A preformed porous sintered mass may be impregnated with molten silver to achieve a similar result.

#### (c) Applications

Sintered electrical contacts based on a tungsten (or molybdenum) carbide-silver mixture are used for certain types of make-and-break contact service.

### 45. Vanadium-Silver

According to Giebelhausen<sup>1</sup> and to Hobson,<sup>2</sup> vanadium and silver do not alloy.

Matsui, Oda, and Naka<sup>3</sup> have studied the conversion rates of sulfur dioxide in the presence of a contact mass which presumably was silver metavanadate on silica gel.

#### (a) Constitution

### 46. Zinc-Silver

Figure 44 is the constitutional diagram for zinc-silver alloys as given by Owen and Edmunds,<sup>1</sup> who have critically reviewed<sup>1, 2, 3</sup> the earlier work of Carpenter and Whiteley,<sup>4</sup> Petrenko and Petrenko,<sup>5</sup> Westgren and Phragmen,<sup>6</sup> Guertler,<sup>7</sup> and Weerts.<sup>8</sup> The phase compositions are given in both weight and atomic per cent, the latter figures appearing in the rectangles.

#### (b) Properties

1. *Physical.* Heycock and Neville<sup>9, 10</sup> observed that the alloy containing about 38 per cent of zinc was sometimes highly colored. If quenched from a temperature of 285 °C or higher, the alloy had a pronounced red color, which disappeared, however, upon heating the specimen to 150 °C. The red color persisted despite attack by sulfuric and hydrochloric acids and alkalis. Although apparently a surface effect, the color appeared even when the alloy was prepared in the presence of hydrogen. The color of the zinc-silver alloys has also been noted by Puschin,<sup>11</sup> Guillet, Petit, and Cournot,<sup>12</sup> and others.





Table 34.—Physical Properties of Wrought Zinc-Silver Alloys.

Silver Content (%)	Vickers An-nealed <sup>1</sup>	Number Cold-rolled <sup>2</sup>	Tensile Strength p. s. i.		Yield Strength* p. s. i.		Elongation (% in 2")		Resistivity microhm-cm (20 °C)	
			An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>	An-nealed <sup>1</sup>	Cold-rolled <sup>2</sup>
0.0	32	36	1,475	8,000	1,475	6,090	3.0	1.5	6.2	6.4
0.99	40	52	3,810	14,750	1,985	13,350	6.0	32.0	6.5	6.5
2.18	49	64	8,600	23,400	3,130	16,600	6.5	24.0	7.0	6.9
6.63	69	76	19,650	31,600	9,070	20,800	11.5	32.0	7.9	8.1
8.59	66	74	27,200	36,000	13,200	24,900	41.0	26.0	8.4	8.6
10.77	67	75	32,100	38,800	20,650	26,500	34.0	26.0	8.8	9.1
15.97	69	86	35,800	45,250	24,200	38,600	26.0	19.0	10.2	10.8

<sup>1</sup> Annealed for 1 hour at 400 °C<sup>2</sup> Cold-rolled 30% 15 B. & S. to 18 B. & S. gauge.

0.2% offset method.

volatile component. A membrane having a porosity of 27.7 volume per cent was produced from a zinc-silver alloy. Read and Kilpatrick<sup>15</sup> have also studied the preparation of such membranes.

The Project has studied the use of the 25-per cent zinc-75-per cent silver alloy as a brazing material. It was found to function quite satisfactorily although its melting range is higher than some of the more commercially used silver brazing alloys.

2. *Chemical.* According to Centnerszwer and Straumanis,<sup>16</sup> the presence of small proportions of silver in zinc, provided other impurities are absent, has very little effect on the solubility rate of zinc in 0.01*N* to 2*N* solutions of hydrochloric and sulfuric acids. Fisher<sup>17</sup> has compared the corrosion of zinc and its alloys with silver, arsenic, antimony, platinum, and lead in 0.5*N* hydrochloric acid, and finds that even with 10 per cent of silver in the alloy, corrosion is not rapid. De Marchi (see Chapter 15) found that, up to the limit of solubility in zinc, silver increased the resistance to corrosion of zinc in a 3-per cent sodium chloride solution. Jordan, Grenell and Herschman<sup>18</sup> found that the silver-rich alloys containing zinc were notably resistant to tarnish which was confirmed by Mathers and Johnson<sup>18</sup> for electrodeposited zinc-silver alloys. The Project observed that the 25-per cent zinc-75-per cent silver brazing alloy was not attacked after a long exposure to sour beer at a boiling temperature.

### (c) Applications

The silver-rich alloys containing about 25 per cent of zinc are used for electrical contacts and for brazing purposes requiring a tarnish resistant, corrosion-resistant alloy of about the same color as silver. Many of the commercially important silver brazing alloys, discussed in Chapter 7, contain a substantial proportion of zinc and silver. The brazing alloy usually contains a substantial percentage of copper as well as of zinc and silver, and may also contain a minor proportion of phosphorus, tin, manganese, cadmium, or nickel. Zinc is being alloyed

commercially with 0.25 to 2.0 per cent of copper and about 0.1 per cent of silver. Both silver and zinc are used in some dental alloys.

#### 47. Zirconium-Silver

According to de Boer<sup>1</sup> zirconium does not dissolve in molten silver. Sykes,<sup>2</sup> however, was able to prepare alloys containing up to 30 per cent of zirconium by melting zirconium powder and silver in a vacuum. Microscopic examination indicated that a compound was formed, probably containing more than 30 per cent of zirconium. The solid solubility of the compound in silver was apparently very slight, and not appreciably affected by temperature. The crystals of the compound were imbedded in a silver-rich matrix, but no eutectic structure was evident. Marden and Rich<sup>3</sup> prepared a zirconium-silver alloy which contained between 10 and 20 per cent of silver, and which, by treatment with acids, yielded finely divided cubical crystals that had a beautiful appearance under the microscope.

Some use appears to be made of a copper alloy, hardened by a few per cent of zirconium and silver.

#### 48. Miscellaneous

A few references appear in the patent literature which relate to some silver alloys concerning which no information has been located in the technical literature.

##### (a) Osmium

It is stated (U. S. Patent 1,248,621) that an alloy consisting of 4 per cent of osmium, 48 per cent of silver and 48 per cent of gold is characterized by a high melting point, great hardness, malleability and ductility, is of low cost and possesses an electrical conductivity comparable to that of platinum. It is suggested as a platinum substitute for magneto contacts.

##### (b) Rhenium

A rhenium-silver alloy is mentioned in British Patent 385,859.

##### (c) Tantalum

Tantalum-silver alloys are mentioned in British Patent 456,018; French Patent 792,568; and German Patents 596,023 and 643,567. The corrosion resistance of tantalum makes the tantalum-silver combination appear interesting.

## Chapter 4

# Ternary and Engineering Alloys Containing Silver

A. J. DORNBLATT AND A. M. SETAPEN \*

### I. INTRODUCTION

This chapter summarizes data obtained by the Project on ternary silver alloys and non-ferrous engineering alloys such as the brasses, bronzes, and light alloys to which a small percentage of silver was added. Data obtained by the Project on binary silver alloys have been summarized in Chapter 3. The compositions of the ternary alloys studied are given in Table 1. Included in this table are some more complex engineering alloys. Minor elements present in some of the commercial alloys have been omitted so that the number of variables could be reduced to a minimum, although it is recognized that the effect of these minor elements is often by no means negligible.

Table 1.—Composition of Ternary Alloys Studied

System	Mark	Composition (% by wt)		
		<i>Al</i>	<i>Mg</i>	<i>Ag</i>
1. <i>Aluminum-Magnesium</i>	H-1	95.57	4.40	—
	H-1A	Rem.	4.40	0.04
	H-1B	Rem.	4.46	0.86
	H-1C	Rem.	4.31	4.10
	H-2	89.77	10.21	—
	H-2A	Rem.	10.04	0.05
	H-2B	Rem.	10.15	0.94
	H-2C	Rem.	9.91	4.39
	H-3	79.76	20.23	—
	H-3A	Rem.	19.83	0.05
	H-3B	Rem.	20.02	0.85
	H-3C	Rem.	18.94	3.88
2. <i>Aluminum-Silicon</i>		<i>Al</i>	<i>Si</i>	<i>Ag</i>
	G-1	97.98	1.98	—
	G-1A	Rem.	1.90	0.87
	G-1B	Rem.	1.90	3.06
	G-1C	Rem.	1.71	4.87
	G-2	95.27	4.67	—
	G-2A	Rem.	4.66	0.05
	G-2B	Rem.	4.53	0.82
	G-2C	Rem.	4.47	4.95
	G-3	87.48	12.47	0.003
	G-3A	Rem.	12.50	0.09
	G-3B	Rem.	12.40	0.82
	G-3C	Rem.	11.72	4.73

\* Silver Research Associate, National Bureau of Standards.

Table 1.—(Continued)

System	Mark	Composition (% by wt)			
		<i>Al</i>	<i>Zn</i>	<i>Ag</i>	
3. Aluminum-Zinc	J-5	Rem.	5.58	—	—
	J-5A	Rem.	5.67	0.12	—
	J-5B	Rem.	5.84	1.30	—
	J-5C	Rem.	4.68	7.10	—
	J-9	Rem.	10.93	—	—
	J-9A	Rem.	11.05	0.07	—
	J-9B	Rem.	11.05	1.16	—
	J-9C	Rem.	10.55	4.80	—
	J-9D	Rem.	8.72	11.30	—
	J-8A	Rem.	20.66	0.10	—
	J-8B	Rem.	19.96	1.52	—
	J-8C	Rem.	19.00	5.72	—
	J-7	68.51	31.31	—	—
	J-7A	Rem.	31.58	0.16	—
	J-7B	Rem.	32.36	1.28	—
	J-7C	Rem.	30.56	6.92	—
4. Copper-Aluminum		<i>Cu</i>	<i>Al</i>	<i>Ag</i>	
	D-5	94.98	5.00	—	—
	D-5A	Rem.	4.82	0.12	—
	D-5B	Rem.	4.48	1.54	—
	D-5C	Rem.	4.05	4.77	—
	D-9	89.50	10.47	—	—
	D-9A	Rem.	10.35	0.10	—
	D-9B	Rem.	10.12	1.15	—
	D-9C	Rem.	9.75	5.16	—
	D-8	84.78	15.19	—	—
	D-8A	84.71	15.16	0.11	—
	D-8B	83.73	15.08	1.14	—
	D-8C	80.21	14.43	5.29	—
5. Copper-Beryllium		<i>Cu</i>	<i>Be</i>	<i>Ag</i>	
	Z-1	97.69	2.26	—	—
	Z-1A	Rem.	2.23	0.11	—
	Z-1B	Rem.	2.19	1.01	—
	Z-1C	Rem.	2.07	4.50	—
	Z-1D	Rem.	1.91	8.85	—
	Z-2	98.82	1.13	—	—
	Z-2A	Rem.	1.11	0.09	—
	Z-2B	Rem.	1.05	1.00	—
	Z-2C	Rem.	1.10	4.76	—
	Z-2D	Rem.	0.93	10.17	—
6. Copper-Manganese-Aluminum		<i>Al</i>	<i>Cu</i>	<i>Mn</i>	<i>Ag</i>
	Y-1	13.46	Rem.	23.24	—
	Y-1C	13.10	Rem.	21.69	5.10

Table 1.—(Continued)

System	Mark	Composition (% by wt)			
7. Copper-Nickel-Phosphorus		Cu	Ni	Ag	P
	H-CA	98.21	1.31	—	0.27
	H-CB	Rem.	1.22	0.11	0.26
	H-CC	Rem.	1.20	0.26	0.27
	H-CD	Rem.	1.40	0.52	0.26
	H-CE	Rem.	1.12	1.03	0.26
	H-CF	Rem.	1.15	5.15	0.24
8. Copper-Nickel		Cu	Ni	Ag	
	A-8	79.73	20.24	—	
	A-8A	Rem.	20.55		0.11
	A-8B	Rem.	20.44		1.44
	A-7	69.42	30.56	—	
	A-7A	Rem.	30.64		0.09
	A-7B	Rem.	30.30		1.17
	A-7C	Rem.	29.18		5.40
	A-3	30	70		—
	A-3A	Rem.	70		0.1
	A-3B	Rem.	70		1
	A-3C	Rem.	70		5
9. Copper-Silicon-Manganese		Cu	Si	Mn	Ag
	X-1	95.84	3.14	1.01	—
	X-1A	Rem.	3.06	1.02	0.10
	X-1B	Rem.	3.11	0.97	1.02
	X-1C	Rem.	3.00	1.08	3.65
10. Copper-Tin		Cu	Sn	P	Ag
	C-5	95.22	4.75		
	C-5A	Rem.	4.64		0.10
	C-5B	Rem.	4.56		1.08
	C-5C	Rem.	4.31		4.63
	C-9	Rem.	9.85		—
	C-0	90.05	9.61		0.001
	CC-0	90.35	9.65	0.071	0.008
	C-9A	Rem.	9.16		0.10
	C-9B	Rem.	9.25		1.20
	C-1	88.17	9.93	Trace	1.89
	CC-1	87.76	9.78	0.044	2.37
	C-6	87.74	9.26		2.85
	C-2	87.33	9.69	0.067	2.88
	CC-2	86.44	10.01	0.043	3.41
	C-3	87.03	9.07	0.056	3.83
	CC-3	85.13	10.11	0.047	4.66
	C-4	85.70	9.20	0.04	4.90
	C-9C	Rem.	8.66		5.83
	C-8	80.02	19.91		—
	CC-8	Rem.	19.87	0.035	0.002
	C-8A	Rem.	19.69		0.10
	C-8B	Rem.	18.81		1.12
	CC-9	78.81	19.31	0.025	1.83
	C-8C	Rem.	18.36		4.18
	CC-10	Rem.	18.75	0.023	4.48

Table 1.—(Continued)

System	Mark	Composition (% by wt)		
		<i>Cu</i>	<i>Zn</i>	<i>Ag</i>
11. <i>Copper-Zinc</i>	B-9	90.36	9.63	—
	B-9A	Rem.	9.62	0.20
	B-9B	Rem.	9.74	1.66
	B-9C	Rem.	8.74	10.48
	BB-8	80.21	19.74	—
	BB-8A	Rem.	19.71	0.10
	BB-8B	Rem.	19.51	1.10
	BB-8C	Rem.	18.68	4.70
	BB-7	70.39	29.58	—
	BB-7A	Rem.	29.31	0.10
	BB-7B	Rem.	28.67	1.10
	BB-7C	Rem.	27.17	5.50
	B-6	60.00	39.95	—
	B-6A	Rem.	39.70	0.11
	B-6B	Rem.	38.59	1.10
12. <i>Lead-Antimony</i>		<i>Pb</i>	<i>Sb</i>	<i>Ag</i>
	U	87.67	11.93	—
	U-A	Rem.	12.08	0.11
	U-B	Rem.	11.93	1.08
	U-C	Rem.	11.45	4.79
13. <i>Lead-Tin</i> (Nominal analysis)		<i>Pb</i>	<i>Sn</i>	<i>Ag</i>
	A <sub>2</sub>	95.0	0.5	4.5
	A <sub>4</sub>	95.0	1.5	3.5
	A <sub>6</sub>	95.0	2.5	2.5
	A <sub>8</sub>	95.0	3.5	1.5
	A <sub>10</sub>	95.0	4.5	0.5
	A <sub>11</sub>	95.0	5.0	0.0
	B <sub>2</sub>	90.0	5.5	4.5
	B <sub>4</sub>	90.0	6.5	3.5
	B <sub>6</sub>	90.0	7.5	2.5
	B <sub>8</sub>	90.0	8.5	1.5
	B <sub>10</sub>	90.0	9.5	0.5
	B <sub>11</sub>	90.0	10.0	0.0
	C <sub>2</sub>	85.0	10.5	4.5
	C <sub>4</sub>	85.0	11.5	3.5
	C <sub>6</sub>	85.0	12.5	2.5
	C <sub>8</sub>	85.0	13.5	1.5
	C <sub>10</sub>	85.0	14.5	0.5
	C <sub>11</sub>	85.0	15.0	0.0
	D <sub>2</sub>	80.0	15.5	4.5
	D <sub>4</sub>	80.0	16.5	3.5
	D <sub>6</sub>	80.0	17.5	2.5
	D <sub>8</sub>	80.0	18.5	1.5
	D <sub>10</sub>	80.0	19.5	0.5
	D <sub>11</sub>	80.0	20.0	0.0

Table 1.—(Continued)

System	Mark	Composition (% by wt)			
		Mg	Sn	Ag	
14. <i>Magnesium-Tin</i>	M-1	93.20	6.61	—	
	M-1A	Rem.	6.43	1.22	
	M-1B	Rem.	6.34	2.82	
	M-1C	Rem.	6.11	4.83	
<i>Magnesium-Tin*</i> (Prepared by Dow Chemical Company)	11919	Rem.	6.15	2.51	
	11920	Rem.	5.79	2.33	
	11921†	Rem.	5.73	2.35	
	11922	Rem.	5.84	—	
	11923	Rem.	5.86	1.38	
	11924	Rem.	5.85	1.82	
15. <i>Magnesium-Zinc</i>		Mg	Zn	Ag	
	L-1	92.85	7.00	—	
	L-1A	Rem.	7.32	0.81	
	L-1B	Rem.	6.96	2.45	
	L-1C	Rem.	7.17	5.12	
	L-2	91.14	8.79	—	
	L-2A	Rem.	9.96	1.34	
	L-2B	Rem.	14.37	3.45	
	L-2C	Rem.	20.39	6.59	
16. <i>Silver-Al-Ti</i>		Ag	Al	Ti	
	NT-1	Rem.	5.93	0.13	
	NT-2	Rem.	6.14	0.14	
	NT-3	Rem.	7.91	0.13	
	NT-4	Rem.	16.23	0.12	
17. <i>Silver-Cu-Si</i>		Ag	Cu	Si	
	V-1	97.27	2.51	0.20	
	V-2	Rem.	4.96	0.47	
	V-3	Rem.	7.47	0.54	
	V-4	Rem.	10.00	0.99	
	V-5	Rem.	3.37	3.78	
18. <i>Silver-Mg-Si</i>		Ag	Mg	Si	Ni
	SMC	Rem.	5.24	1.28	
	SSC	Rem.	1.19	0.79	0.05
19. <i>Silver-Mn-Si</i>		Ag	Mn	Si	Ni
	WX-A	Rem.	19.55	0.06	
	WX-B	Rem.	17.12	0.15	
	WX-C	Rem.	16.29	0.20	0.81
	WX-D	Rem.	15.97	0.43	
	WX-E	Rem.	13.60	0.36	
	WX-F	Rem.	7.65	0.90	
20. <i>Silver-Si-Ni</i>		Ni	Si	Ag	
	S-X	0.06	0.23	Rem	
	SS-B	0.07	0.87	Rem	

\*All alloys contain 0.5% Mn

†11921 also contains 3.09% Al



Attention was largely devoted to ascertaining the significant effects of a silver addition ranging from 0.1 to 5.0 per cent in binary non-ferrous alloys of the industrially important types. This range of silver additions was selected on the assumption that, in most applications, the metal cost is only a small fraction of the cost of the finished commodity after allowing for such items as rolling, machining, assembling, etc. Consequently the addition of even 5 per cent of silver, worth about five dollars a pound, representing an additional metal cost of 25 cents a pound, would not be commercially impracticable if there were sufficient improvement in the alloy. Larger percentages of silver would probably not be considered in engineering alloys used on a tonnage basis.

With the exception of the silver-rich alloys, the melts were usually prepared by induction-melting in 15 to 60 pound lots. The metal was cast into chill molds, and all the alloys in a given series were poured at the same temperature. Aging studies were carried out by B. S. Old at the Massachusetts Institute of Technology on material which generally had been reduced by rolling from a thickness of 1.0 inch to 0.25 inch. Physical-property data were obtained at the National Bureau of Standards on wrought material usually of No. 15 (0.057-inch) or No. 18 (0.040-inch) B. & S. gauge. Attention was also directed to the possible effect of silver on castability, grain size, recrystallization or annealing temperature, machinability and color. Data obtained by V. S. de Marchi at Columbia University on the effect of silver on the resistance of the

Table 2.—Hardness of Chill-Cast Aluminum-Magnesium-Silver Alloys.

Alloy	Hardness	
	Brinell Number	Rockwell E Number
H-1	45	52
H-1A	48	60
H-1B	53	65
H-1C	68	81
H-2	69	83
H-2A	72	85
H-2B	75	86
H-2C	80	87
H-3	114	104
H-3A	96	99
H-3B	79	92
H-3C	90	95

alloys to corrosion are reviewed in Chapter 15, where some additional data are also given on the resistance of a few of the silver-rich alloys to corrosion, as determined by J. M. Thomas at Lehigh University. The resistance of the silver-rich alloys to tarnish was noted by the Project, as summarized in Table 11 of Chapter 15.

Attention is called to the bibliography and patent references relating to alloys in Appendix I, Section B and Appendix II, Section 2.

## II. ALLOYS INVESTIGATED

## 1. Aluminum-magnesium Alloys

Alloys containing 4.4 to 20.2 per cent magnesium and 0.04 to 4 per cent of silver were studied. The 4-per cent magnesium series could be hot-worked, but the 10- and 20-per cent magnesium series were too brittle to work. Table 2 summarizes the hardness data determined on the chill-cast alloys. Silver is an effective hardener in the alloy with the lowest magnesium content. The castability of the 4-per cent magnesium alloy appeared to be adversely affected by the addition of silver in the

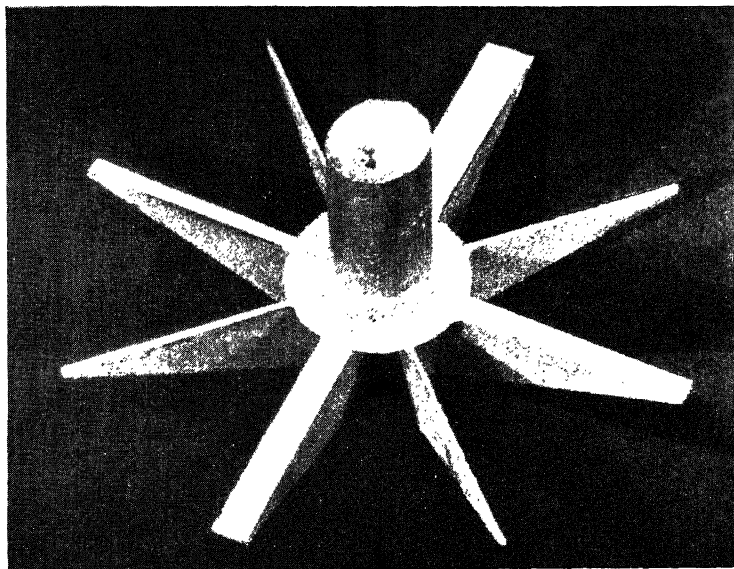


FIGURE 1. Castability test specimen.

Magnification  $\times 4/5$ . This example is a sand-cast alloy containing 50% Bi, 26.7% Pb, 13.3% Sn, 10% Cd, which melts at 70 °C and was cast at 259 °C. Rating is 100% since all fins are completely reproduced.

amounts of 1 and 5 per cent. The castability was measured by the extent to which the metal filled the various radial fins of the test casting shown in Figure 1. The thickness of the various fins, in sixty-fourths of an inch, was 1, 2, 3, 4, 8, 12, 16, and 25. If the casting completely filled all fins, it was given a rating of 100 per cent, and a correspondingly lower rating if the casting did not completely fill all fins.

The response of these alloys to precipitation heat-treatment is summarized in Table 3. No aging was detected in the silver-free alloy (H-1)

Table 3.—Aging Properties of Aluminum-Magnesium-Silver Alloys.<sup>1</sup>

Alloy	Condition	Hardness (Rockwell No.)—		Aging	
		Quenched	Aged	Time (hours)	Temp. (°C)
H-1	Wrought <sup>2</sup>	3	3	—	—
H-1A	Wrought <sup>2</sup>	3	3	—	—
H-1B	Wrought <sup>2</sup>	60F	69F	5.25	175
H-1C	Wrought <sup>2</sup>	55F	76F	5.75	175
H-2	Wrought <sup>2</sup>	33B	59B	5.5	245
H-2A	Wrought <sup>2</sup>	44B	66B	4	245
H-2B	Wrought <sup>2</sup>	37B	61B	4	245
H-2C	Wrought <sup>2</sup>	38B	51B	5.5	245
H-3	Cast	61B	84B	4	245
H-3A	Cast	57B	80B	2	245
H-3B	Cast	38B	60B	5.5	245
H-3C	Cast	59B	76B	5.5	245

<sup>1</sup> Alloys were homogenized 49 hours at 425 °C, water-quenched, and aged at the temperatures indicated.

<sup>2</sup> Hot-forged at 400 °C.

<sup>3</sup> No aging detected.

Table 4.—Hardness Conversion Table (Approximate).

Brinell Number 500 or 3000 Kg Load	Rockwell B Scale	Rockwell E Scale	Rockwell F Scale	Vickers Number
242	100	115	114	242
235	99	114	113	235
228	98	113	112	228
222	97	113	112	222
216	96	112	111	216
210	95	112	111	210
205	94	111	110	205
200	93	111	110	200
195	92	110	109	195
190	91	110	109	190
185	90	109	108	185
180	89	109	108	180
175	88	108	107	175
170	86	107	106	170
165	85	107	105	165
160	83	106	104	160
155	82	105	104	155
150	80	104	103	150
145	78	103	101	145
140	76	102	100	140
135	74	101	99	135
130	72	100	98	130
125	70	99	97	125
120	67	98	95	120
115	64	96	94	115
110	62	95	93	110
105	58	93	90	105
100	55	92	89	100
95	51	89	86	95
90	48	88	85	90
85	44	85	83	85
80	40	83	81	80
75	35	80	78	75
70	27	75	73	70
65	21	71	70	65
60	10	63	64	60
57	1	56	59	57

containing 4.4 per cent of magnesium; some precipitation-hardening was noted when the alloy (H-1B) contained 0.86 per cent of silver, and a more substantial increase in hardness was produced by heat-treating the 4-per cent silver alloy (H-1C). Both the 10- and 20-per cent magnesium alloy controls (H-2 and H-3) were precipitation-hardenable, and the addition of silver did not impart additional hardenability under the conditions noted. The somewhat low hardness number for the H-3B alloy as compared to the other alloys with about 20 per cent of magnesium was not confirmed by tests made on a second ingot from the same heat. Instead of a Brinell number of 79 (Table 2) the hardness of the chill-cast alloy ranged from 100 to 114 Brinell number.

Table 4 is a conversion table suitable for making approximate comparisons of hardness data obtained by different testing procedures.

The results of the corrosion tests on these alloys indicated that the presence of about 4 per cent of silver increased their corrosion by a 3 per cent sodium chloride solution, but that with less than about 1 per cent of silver, their corrosion resistance was not substantially altered. This is an indication that the smaller amount of silver was retained in solution, whereas the larger amount existed as a silver-rich phase which induced galvanic attack.

## 2. Aluminum-silicon Alloys

The effect of silver on the hardness of chill-cast, annealed, and cold-rolled aluminum alloys containing about 2.5, 5, and 12.5 per cent of silicon (G-1, G-2, and G-3 series) is indicated in Table 5. Less than

Table 5.—Hardness of Aluminum-Silicon-Silver Alloys.

Alloy	Chill-cast		Annealed <sup>1</sup> Vickers Number	Cold rolled <sup>2</sup> Vickers Number
	Brinell Number	Rockwell E Number		
G-1	27	5	24	47
G-1A	27	5	25	50
G-1B	38	42	30	59
G-1C	41	46	40	71
G-2	34	23	28	53
G-2A	34	24	28	51
G-2B	34	22	30	55
G-2C	44	51	40	74
G-3	46	52	36	62
G-3A	45	53	35	64
G-3B	46	52	35	64
G-3C	67	75	39	83

<sup>1</sup> One hour at 350 °C (No. 15 B. & S. gauge sheet).

<sup>2</sup> From No. 15 to No. 18 gauge.

1 per cent of silver had no appreciable effect on the hardness of these alloys, but the samples containing from 3 to about 5 per cent of silver were of superior hardness. Annealing tests conducted on material that had been worked down to number 15 B. & S. gauge showed that the alloys

containing the largest percentage of silver did not lose in hardness even when annealed for six hours at 200 °C, whereas the silver-free controls all suffered substantial losses in hardness by this treatment. While the alloys of highest silver content in each group were softened to some extent at 250 °C, the hardness values of the fully annealed specimens were still well above those for the control alloys. This signifies that about 4 or 5 per cent of silver improves the properties of these alloys at moderately elevated temperature. The G-1C, G-2C, and G-3C alloys

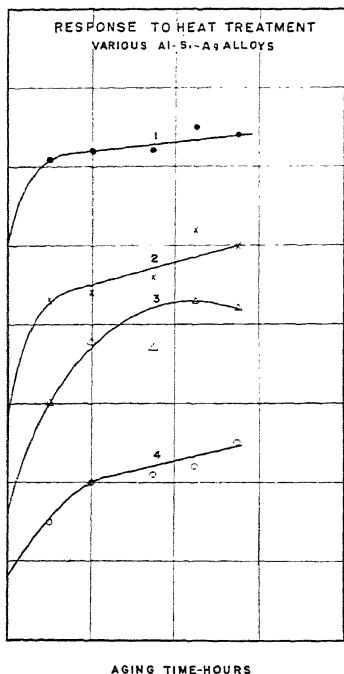


FIGURE 2.

Response to heat treatment of various aluminum-silicon-silver alloys.

Curve 1. Alloy G-3C: 11.72% silicon, 4.73% silver.

Curve 2. Alloy G-2C: 4.47% silicon, 4.95% silver.

Curve 3. Alloy G-1C: 1.71% silicon, 4.87% silver.

Curve 4. Alloy G-1B: 1.90% silicon, 3.06% silver.

All alloys solution-treated 47 hours at 520 °C, quenched in water, and aged at 150 °C.

each showed an increase in hardness on annealing at 350 °C for 6 hours, or for one hour at 400 °C, followed by cooling in air from the annealing temperature.

The tendency of the latter alloys toward precipitation-hardening is indicated by Figure 2, which shows the increase in hardness of the chill-cast samples, produced by aging at 150 °C for the indicated periods of time after a solution-treatment at 520 °C. Additional data on the aging properties of the alloys are given in Table 6. It will be noted that aging was not detected in the alloys that contained no silver (the trace of silver

Table 6.—Aging Properties of Chill-Cast Aluminum-Silicon-Silver Alloys.<sup>1</sup>

Alloy	Hardness		Aging Time (hours)
	Quenched Rockwell F Number	Aged Rockwell Number	
G-1	2	2	—
G-1A	2	2	—
G-1B	8	25	3.75
G-1C	16	43	2.25
G-2	2	2	—
G-2A	2	2	—
G-2B	2	2	—
G-2C	28	52	2.25
G-3	2	2	—
G-3A	2	2	—
G-3B	2	2	—
G-3C	50	65	2.25

<sup>1</sup> Alloys were homogenized 47 hours at 520 °C, quenched in water, and aged at 190 °C.

<sup>2</sup> No aging detected.

in alloy G-3 of Table 1 was present in the aluminum ingot and is a normal impurity).

The corrosion test data show that the alloys containing enough silver to improve their hardness were less resistant to corrosion than the controls.

The eutectic aluminum-silver alloy is employed in low-expansion pistons, and the additions of silver to such an alloy may well be advantageous, as greater hardness and better retention of strength and hardness at elevated temperature may be expected. In this application there is no

Table 7.—Hardness of Aluminum-Zinc-Silver Alloys.

Alloy	Chill Cast Brinell Number	Annealed <sup>1</sup> Vickers Number	Annealing Temp. (°C)	Cold-rolled <sup>2</sup> Vickers Number
J-5	19	25	350	39
J-5A	22	25	350	43
J-5B	37	31	350	53
J-5C	57	61	350	96
J-9	33	35	300	70
J-9A	34	40	300	71
J-9B	53	45	300	85
J-9C	74	60	300	95
J-9D	83	70	300	100
J-8	77	—	—	—
J-8A	83	78	300	122
J-8B	89	76	300	134
J-8C	100	64	300	84
J-7	93	83	200	142
J-7A	93	85	200	121
J-7B	93	87	200	139
J-7C	86	91	200	124

<sup>1</sup> One hour at indicated temperature (No. 18 B. & S. gauge sheet).

<sup>2</sup> From No. 15 B. & S. to No. 18 B. & S. gauge.

problem of galvanic corrosion, and the cost of the silver is not of controlling importance. Considerable use is made of aluminum-silicon alloys containing about 5 per cent of silicon for applications where ease of casting and lightness are the primary considerations. Although similar alloys containing a little copper or magnesium are also improved by heat-treatment, the additional hardness imparted by silver might be of some interest.

### 3. Aluminum-zinc Alloys

The effect of silver in aluminum-zinc alloys containing from 5 to 30 per cent of zinc is summarized in Table 7, and the aging properties of

Table 8.—Aging Properties of Hot-Forged Aluminum-Zinc-Silver Alloys.<sup>1</sup>

Alloy	Hardness (Rockwell F No.)		Aging Time (hours)
	Quenched	Aged	
J-5	- 31	- 21	10
J-5A	- 29	- 1	24
J-5B	- 4	19	10
J-5C	50	63	3.5
J-9	21	65	3
J-9A	30	66	24
J-9B	26	73	6
J-9C	70	89	24
J-9D	90	94	3
J-S	—	—	—
J-8A	52	88	2
J-8B	74	96	2
J-8C	90	104	2

<sup>1</sup> Alloys were homogenized 49 hours at 490 °C, quenched in water, and aged at room temperature.

the same alloys in Table 8. It appears from these data that the increase in hardness conferred by silver can be obtained more economically by increasing the zinc in the alloy by approximately the same amount. Evidence of precipitation-hardening was noted in examining annealing

Table 9.—Hardness of Aluminum-Zinc-Silver Alloys After Heating at Indicated Temperature for 6 Hours Followed by Cooling in Air.

Alloy	Hardness Vickers Number	Temperature (°C)
J-5C	71	400
J-9C	90	400
J-9D	79	400
J-8A	78	400
J-8B	108	400
J-8C	60	400
J-7	142	300
J-7A	142	300
J-7B	137	300
J-7C	122	400
J-7C	86	300

curves obtained on some of the alloys, in that a minimum in hardness occurred at a particular temperature, and the hardness increased on air-cooling from an annealing temperature higher than this. This effect was observed in the J-5C alloys containing 5.5 per cent of zinc and 7.1 per cent of silver, in the J-9 alloys containing 4.8 per cent and 11.3 per cent of silver, and in all alloys of the J-8 and J-7 series. It is not known whether or not the alloys exhibit any of this higher hardness while at the elevated temperature, or if the higher hardness is the result of room-temperature aging subsequent to the "annealing" treatment. Table 9 summarizes data obtained on the hardness of all alloys of this class which hardened after air-cooling from the annealing temperature. The data extend to 400 °C, and the values given are the maximum obtained. In the J-9, J-8, and J-7 series, the highest silver alloy did not exhibit the highest hardness. However, the data for J-7C in Table 9 leads one to conclude that the alloys of higher silver content require a higher temperature (or a longer aging period) to attain maximum hardness.

The presence of silver in the aluminum-zinc alloys reduced their resistance to corrosion by 3-per cent sodium chloride solution.

#### 4. Copper-aluminum Alloys (Aluminum Bronzes)

Some effects produced by adding silver to a group of copper-aluminum alloys have been studied. Silver was added to the copper-aluminum binary mixture, although the commercial aluminum-bronzes contain a small proportion of other elements, such as iron, which may markedly

Table 10.—Hardness of Copper-Aluminum-Silver Alloys.

Alloy	Chill-cast		Annealed <sup>1</sup> Vickers Number	Annealing Temp. (°C)	Cold-rol Vicke Numb
	Brinell Number	Rockwell Number			
D-5	45	64E	105	500	179
D-5A	42	46E	104	500	181
D-5B	50	58E	127	500	188
D-5C	55	70E	166	500	197
D-9	113	80B	157	610	256
D-9A	116	79B	153	610	255
D-9B	109	80B	141	610	256
D-9C	113	82B	164	610	255
D-8	331	112B	55C		
D-8A	388	112B	57C		
D-8B	388	114B	57C		
D-8C	375	112B	57C		

<sup>1</sup> One hour at indicated temperature (No. 18 B. & S. gauge sheet).

<sup>2</sup> From No. 15 B. & S. to No. 18 B. & S. gauge.

affect the physical properties of the industrial product. The effect of silver on the hardness of the aluminum bronzes investigated is summarized in Table 10. Physical-property data were obtained on the 5- and 10-per cent aluminum (D-5 and D-9) series of alloys which had been rolled to sheet. These data are summarized in Table 11, which also



Table 11.—Effect of Composition and Heat Treatment on Properties of Copper-Aluminum-Silver Alloys.

Alloy†	Hardness Rockwell Number	Tensile Strength p. s. i.	Yield Strength* p. s. i.	Proportional limit p. s. i.	Elongation (% in 2")	Resistivity microhm-cm (20 °C)
Specimens prepared from cold-rolled sheets heated at 400 °C for 6 hours						
D-5	81F	60,600	27,200	17,100	60	10.0
D-5A	79F	60,550	27,750	17,250	59	10.6
D-5B	89F	65,250	36,600	20,700	52	9.7
D-5C	99F	68,100	49,250	29,050	42	9.7

Specimens heated 16 hours at 900 °C, water quenched, and aged 6 hours at 400 °C.

D-5	50F	47,000	8,700	4,590	67	
D-5A	50F	46,400	7,900	4,010	62	
D-5B	52F	45,400	9,600	5,930	60	
D-5C	95F	59,500	43,000	33,550	43	

Specimen prepared from cold-rolled sheets heated at 600 °C for 6 hours

D-9	86B	80,700	45,450	20,700	11	13.5
D-9A	81B	68,100	43,500	16,250	7	12.4
D-9B	84B	75,900	47,000	29,500	8	12.9
D-9C	83B	71,900	46,600	23,150	9	12.6

\* 0.2% offset method.

† All specimens were 0.05S" thick.

shows the effect of heat-treatment on the D-5 series of alloys. The response to heat-treatment of the D-5C alloy is also shown in Figure 3. The presence of 4.7 per cent of silver has made the D-5 alloy precipitation-hardenable but age-hardening was not detected in the case of the D-5, D-5A or D-5B alloys. The effect of heat-treatment on the 10- and

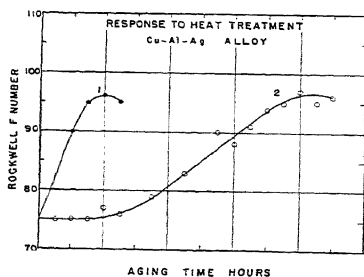


FIGURE 3.

Response to heat treatment of a copper-aluminum-silver alloy.

Alloy D-5C: 4.05% aluminum, 4.77% silver, remainder copper.

Homogenized 48 hours at 700 °C, then heated to 750 °C for one hour, and quenched in water. Curve 1, aged at 475 °C; Curve 2, aged at 400 °C.

15-per cent aluminum bronzes (D-9 and D-8 series) was not determined, although it is known, of course, that the properties of commercial aluminum bronzes containing about 10 per cent of aluminum can be markedly changed by heat treatment.

From the data of Table 11, it is apparent that the presence of 4.7 per cent of silver in the aluminum bronze containing about 5 per cent of aluminum markedly improved the yield strength of the alloy with little sacrifice in ductility. It will be noted, too, that the alloys of lower silver

content with comparable aluminum content did not respond favorably to heat-treatment. The properties of the D-5C alloy compared very favorably with those of the D-9 alloy, which, however, had inferior ductility.

The effect of silver on the annealing characteristics of the D-5 series of alloys is shown in Figure 4. It will be noted that, with 1.5 per cent of silver in the alloy, the annealing temperature was raised about 50 °C. Further increase in silver raised the annealing temperature a little more. It was found that, under similar annealing conditions, silver did not significantly increase the annealing temperature of the D-9 alloy, but the D-9 series required a higher annealing temperature than did the

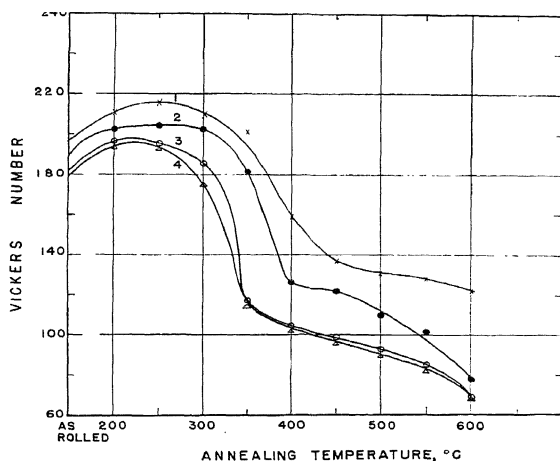


FIGURE 4. Effect of silver on the annealing characteristics of a copper-aluminum alloy.

- Curve 1. Alloy D-5C: 4.05% aluminum, 4.77% silver, remainder copper.  
 Curve 2. Alloy D-5B: 4.48% aluminum, 1.54% silver  
 Curve 3. Alloy D-5A: 4.82% aluminum, 0.12% silver  
 Curve 4. Alloy D-5: 5.00% aluminum, remainder copper

Annealing time, 6 hours. Material cold-rolled from No. 15 to No. 18 B. & S. gauge.

D-5 series. Recrystallization occurred in the range of 350 to 450 °C in alloys of the D-9 series. Silver had a moderate grain-refining effect in all the aluminum bronzes, the effect being noticeable with about 0.1 per cent of silver and increasing with increasing silver content.

According to de Marchi's data, the corrosion resistance of the D-5 series of alloys was not significantly altered by the addition of silver. There was an indication that silver improved the resistance of the 10-per cent aluminum bronze to sodium chloride (brine) corrosion.

### 5. Copper-beryllium Alloys (Beryllium Bronzes)

The precipitation-hardenable alloy of copper containing about 2.25 per cent of beryllium has unusually high physical properties for a non-ferrous alloy, and is known to the trade as beryllium bronze. Cobalt,

Table 12.—Aging Properties of Wrought Copper-Beryllium-Silver Alloys.<sup>1</sup>

Alloy	—Hardness (Rockwell B No.)—		Aging Time (hours)
	Quenched	Aged	
Z-1	53	112	4.5
Z-1A	54	111	4.5
Z-1B	52	112	4.5
Z-1C	52	109	4.5
Z-1D	60	108	4.5
Z-2	8		
Z-2A	9		
Z-2B	12		
Z-2C	32	100	17
Z-2D	32	99	17

<sup>1</sup>Alloys were homogenized 25 hours at 780 °C, quenched in water, and aged at 250 °C.

<sup>2</sup>No aging detected.

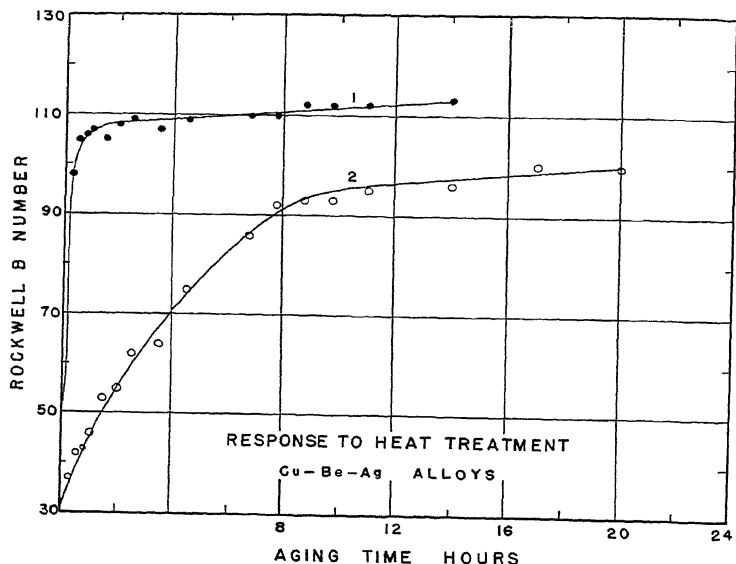


FIGURE 5. Response to heat treatment of copper-beryllium-silver alloys.

Curve 1. 2.25% beryllium, 97.25% copper alloy.

Curve 2. 1.10% beryllium, 4.76% silver, remainder copper.

Alloys cold-rolled 30%, then homogenized at 780 °C for 25 hours, quenched in water, and reheated in a salt bath at 290 °C for the indicated period of time.

for example, can be used in beryllium bronzes as a substitute for about one per cent of the more costly beryllium. It was decided to observe the effect of silver on beryllium bronze to determine whether or not it might be substituted for the more expensive beryllium, or impart some other benefit. Two series of alloys were therefore prepared. One series, the Z-1 group, comprised  $2\frac{1}{4}$  per cent beryllium-copper containing various increments of silver; the Z-2 group was similarly based on a 1.1 per cent beryllium-copper alloy.

The aging properties of the wrought alloys are illustrated by the data of Table 12. Silver ranging from 0.1 to 8.8 per cent had no noticeable effect on the aging properties of the Z-1 alloy. The beryllium content of the Z-2 alloy was apparently too low to cause precipitation-hardening, but the Z-2C alloy which also contained 4.76 per cent of silver exhibited hardening properties comparable to those of the Z-1 alloy. This is confirmed in Figure 5 in which the data for all alloys of the Z-1 series, within the experimental limits, are represented by curve 1 and similarly the data for the Z-2C and Z-2D alloys by curve 2.

Additional data indicative of the aging properties of these alloys are given in Table 13, together with data on the hardness of the chill-cast alloys.

Table 13.—Hardness of Copper-Beryllium-Silver Alloys.

Alloy	Chill-cast		Vickers Number		
	Brinell Number	Rockwell B Number	Cold-rolled <sup>1</sup>	Reheated	Reheated <sup>4</sup>
Z-1	109	75	232	400 <sup>2</sup>	162
Z-1A	104	75	236	383 <sup>2</sup>	162
Z-1B	119	81	224	393 <sup>2</sup>	158
Z-1C	118	82	—	—	—
Z-1D	130	86	—	—	—
Z-2	67	35	167	219 <sup>2</sup>	79
Z-2A	67	29	169	222 <sup>2</sup>	79
Z-2B	65	36	168	223 <sup>2</sup>	77
Z-2C	74	47	—	—	—
Z-2D	91	61	—	—	—

<sup>1</sup> Water-quenched from 780 °C and cold-rolled 30 per cent (No. 15 B. & S. to No. 18 B. & S. gauge).

<sup>2</sup> 250 °C for 5.5 hours after <sup>1</sup>.

<sup>3</sup> 350 °C for 5.5 hours after <sup>1</sup>.

<sup>4</sup> 550 °C for 5.5 hours after <sup>1</sup>.

Some data on the physical properties of these alloys are summarized in Table 14. During the 780 °C homogenizing, or solution treatment, the furnace happened to reach a temperature of 815 °C and all the tensile specimens containing 4.5 per cent or more of silver were ruined because of the melting of some intergranular constituent, fusible at this temperature. For this reason no tensile data were obtained on the Z-1C, Z1-D, Z-2C, and Z-2D alloys. At the prevailing market prices for silver and beryllium, at the time of this work, the cost of the 4.5 per cent of silver required was about the same as that of the 1 per cent of beryllium which

Table 14.—Physical Properties of Some Copper-Beryllium-Silver Alloys.

Alloy	Hardness (Vickers Number)	Tensile Strength p. s. i.	Yield* Strength p. s. i.	Elongation (% in 2")	Resistivity microhm-cm (20 °C)
0.05S" specimens heated for 6 hours at 780 °C, water-quenched, and reheated for 5.5 hours at 250 °C.					
Z-1	323	151,000	115,200	4.0	10.1
Z-1A	315	153,500	112,400	4.0	10.2
Z-1B	323	152,000	108,100	7.0	10.4
Z-1C	—	—	—	—	10.1
Z-1D	—	—	—	—	8.9
0.05S" specimens heated for 6 hours at 780 °C, water-quenched, and reheated for 3 hours at 350 °C.					
Z-2	73	43,700	13,830	54.0	6.3
Z-2A	72	45,300	15,900	51.0	6.6
Z-2B	78	46,900	18,950	46.0	6.7
Z-2C	—	—	—	—	6.6
Z-2D	—	—	—	—	6.2

\*0.2% offset method.

it could replace; hence it was decided to pursue this investigation no further.

Studies showed that the annealing temperature of the binary copper-beryllium alloys was not significantly raised by the addition of silver in the range investigated. Examination of de Marchi's data on the corrosion of the alloys in 3-per cent sodium chloride solution shows no substantial change in their corrosion resistance.

#### 6. Copper-manganese-aluminum Alloy (Heusler's Alloy)

The effect of adding about 5 per cent of silver to the magnetic copper-manganese-aluminum alloy known as Heusler's alloy was observed qualitatively. Alloy Y-1C was found to be magnetic, hard and brittle. It cast better than alloy Y-1, which was of similar composition except for the absence of silver. The hardness of the chill-cast alloys was recorded; for the Y-1 and Y-1C alloys the hardness values were, respectively, Rockwell C 57 and Rockwell C 52.

#### 7. Copper-nickel-phosphorus Alloys (High-conductivity Bronzes)

The properties of copper-rich alloys of the copper-nickel-phosphorus system have been studied and recently discussed by D. K. Crampton, H. L. Burghoff, and J. T. Stacy.\* Because of the high strength and good electrical conductivity of certain of these alloys, it was decided to investigate the effect of silver upon their properties. Table 15 summarizes the results of hardness tests made on samples of chill-cast alloys of the H-C series. A substantial improvement in hardness was produced by heat-treatment, but silver did not materially alter the response of the alloy to the heat treatment. Table 16 summarizes data obtained on the

\* (Tech. Publ. No. 1142, Amer. Inst. Min. and Met. Eng., February, 1940.)

Table 15.—Hardness and Aging Properties of Cast Copper-Nickel-Phosphorus Alloys Containing Silver.

Alloy	As Cast Rockwell F Number	Homogenized <sup>1</sup> Rockwell F Number	Aged <sup>2</sup> Rockwell Number
H-CA	79	50	67
H-CB	79	52	68
H-CC	76	51	65
H-CD	78	51	64
H-CE	76	51	63
H-CF	81	64	71

<sup>1</sup> Homogenized 20 hours at 760 °C and water-quenched.<sup>2</sup> Aged 4 hours at 455 °C.

physical properties of these alloys in the wrought condition. The effect of various heat treatments is also indicated by the data of Table 16.

The H-CF alloy, containing 5.1 per cent of silver, had about thirty per cent higher yield strength and about 16 per cent less conductivity than the silver-free alloy, H-CA, after precipitation-hardening. Its hardness and strength also surpassed the corresponding properties of the H-CA alloy, and the ductility, as measured by the elongation, was of about the same order of magnitude. Similar superiority was noted in the heat-treated and cold-rolled condition. However, the improvement is

Table 16.—Physical Properties of Wrought Copper-Nickel-Phosphorus Alloys Containing Silver.

Alloy†	Hardness—		Tensile Strength p. s. i.	Yield* Strength p. s. i.	Elongation (% in 2")	Resistivity microhm-cm (20 °C)
	Vickers Number	Rockwell Number				
Specimens annealed 1 hour at 760 °C and water-quenched.						
H-CA	58	73R <sub>H</sub>	38,300	10,500	46	5.4
H-CB	60	79R <sub>H</sub>	38,700	15,600	38	5.6
H-CC	58	74R <sub>H</sub>	38,700	13,200	42	5.5
H-CD	60	81R <sub>H</sub>	39,100	10,550	46	5.4
H-CE	61	83R <sub>H</sub>	40,200	11,700	41	5.5
H-CF	76	88R <sub>H</sub>	47,000	16,400	48	5.3
Specimens annealed 1 hour at 760 °C, water-quenched, and aged 2 hours at 455 °C.						
H-CA	127	72R <sub>B</sub>	63,800	45,400	25	2.8
H-CB	118	71R <sub>B</sub>	62,800	44,200	30	2.7
H-CC	122	69R <sub>B</sub>	62,700	43,900	30	2.9
H-CD	129	72R <sub>B</sub>	63,000	43,600	33	2.7
H-CE	132	70R <sub>B</sub>	64,100	46,000	26	2.8
H-CF	157	83R <sub>B</sub>	70,200	61,400	20	3.3
Specimens annealed 1 hour at 760 °C, water-quenched, aged 2 hours at 455 °C and cold rolled 20%.						
H-CA	159	83R <sub>B</sub>	74,450	71,350	10	2.9
H-CB	161	83R <sub>B</sub>	73,550	70,000	10	2.8
H-CC	162	84R <sub>B</sub>	74,700	70,350	13	2.8
H-CD	161	84R <sub>B</sub>	75,750	72,150	14	2.8
H-CE	160	83R <sub>B</sub>	75,750	69,900	10	3.1
H-CF	180	88R <sub>B</sub>	81,600	77,500	9	3.3

\* 0.2% offset method.

† All specimens were 0.10" thick.

not commensurate with the increase in cost of the alloy. Silver to the amount of one per cent or less had no significant effect on the alloy.

Annealing studies showed that silver did not affect the annealing characteristics of the H-CA alloy.

### 8. Copper-nickel Alloys

The composition of the copper-nickel alloys studied is given in Table 1. Despite the fact that only fragmentary data could be obtained owing to difficulty in working these alloys, some of the results were very interesting. The effect of silver on the hardness of the chill-cast alloys is summarized in Table 17. In the 80-20 copper-nickel group (A-8

Table 17.—Hardness of Copper-Nickel-Silver Alloys.

Alloy	As Cast		Annealed <sup>1</sup> Vickers Number	Cold-rolled <sup>2</sup> Vickers Number
	Brinell Number	Rockwell Number		
A-8	58	70E	69	151
A-8A	74	80E	104	182
A-8B	84	86E	116	197
A-7	77	82E	118	194
A-7A	84	83E	122	203
A-7B	84	86E	129	208
A-7C	88	89E	129	210
A-3	104	77B	—	—
A-3A	106	77B	—	—
A-3B	93	67B	—	—
A-3C	93	67B	—	—

<sup>1</sup> Cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge and heated 5.5 hours at 610 °C.

<sup>2</sup> From No. 15 B. & S. to No. 18 B. & S. gauge.

series) of alloys, silver was quite effective in increasing the hardness. It had much less effect on the harder 70-30 group (A-7 series) of alloys, and appeared actually to soften the 30-70 copper-nickel (A-3 series) alloy when present to the extent of 1 per cent.

The effect of silver on the physical properties of some of the copper-nickel alloys is summarized in Table 18. The improvement in the 80-20

Table 18.—Physical Properties of Wrought Copper-Nickel-Silver Alloys.

Alloy†	Hardness Vickers Number	Tensile Strength p. s. i.	Yield strength* p. s. i.	Elongation (% in 2")	Resistivity microhm-cm (20 °C)
A-8	70	45,300	18,900	27	25.5
A-8A	107	51,000	30,200	25	26.9
A-8B	—	—	—	—	27.1
A-7	119	64,700	35,100	25	36.5
A-7A	127	64,600	37,100	23	39.0
A-7B	—	—	—	—	38.9
A-7C	—	—	—	—	33.1

\* 0.2% offset method.

† Cold-rolled specimens heated for 6 hours at 600 °C. Specimens 0.058" thick.

alloy produced by 0.1 per cent of silver (A-8A alloy) is notable. Annealing studies showed that the annealing temperature of the A-8A alloy is about 50 °C higher than that of the A-8 alloy, but it is unlikely that the improvement in strength shown in Table 18 can be attributed to incomplete annealing of the cold-worked sheet. The annealing studies showed that about 0.1 per cent of silver produced the largest proportionate effect on the annealing temperature of the 80-20 alloy, further amounts being of little greater benefit, and that silver up to 5.4 per cent did not appreciably alter the annealing characteristics of the 70-30 copper-nickel alloy.

Alloys of the A-8 and A-7 groups containing up to 1.4 per cent of silver failed to show any response to precipitation-hardening treatments. However, alloy A-7C, containing 5.4 per cent of silver, did age-harden from Rockwell F 78 to Rockwell F 90 after a solution treatment at 800 °C and aging for 1½ hours at 450 °C.

The castability of the 80-20 alloys was not appreciably altered by silver additions, but in the case of the 70-30 alloy, the castability was distinctly improved by adding as little as 0.1 per cent of silver. The addition of larger proportions of silver to the 70-30 copper-nickel alloy caused a small additional improvement. Castability data were not obtained on the 30-70 copper-nickel alloy.

It was found that the A-3B and A-3C alloys machined much better than did the A-3 or A-3A alloys. Similarly, the machinability of the A-8C and A-7C alloys was superior to that of the silver-free A-8 and A-7 alloys. The silver-containing alloys of the A-7 series appeared to work better than the silver-free A-7 alloy, the improvement being most noticeable with the higher content of silver.

Low corrosion loss in the case of all alloys of the A-7 and A-8 series was reported by de Marchi.

From the data cited above, it appears that the possibility of improving the copper-nickel alloys by the addition of a small percentage of silver warrants commercial investigation.

## 9. Copper-silicon-manganese Alloys

The copper-silicon-manganese alloy X-1, of composition listed in Table 1, represents a commercially important type of corrosion-resistant bronze frequently used in welded assemblies and in rolled sheet form.

Table 19.—Hardness of Copper-Silicon-Manganese Alloys Containing Silver.

Alloy	Chill Cast Brinell Number	Annealed <sup>1</sup> Vickers Number	Cold-rolled <sup>2</sup> Vickers Number
X-1	57	98	189
X-1A	60	93	190
X-1B	62	94	197
X-1C	69	129	211

<sup>1</sup> Cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge and heated 6 hours at 600 °C.

<sup>2</sup> From No. 15 B. & S. to No. 18 B. & S. gauge.



The effect of silver on the hardness of the alloy is shown in Table 19 and on some other properties in Table 20.

Table 20.—Physical Properties of Copper-Silicon-Manganese Alloys Containing Silver.

Alloy†	Hardness Vickers Number	Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elongation (% in 2")	Resistivity Microhm-cm (20 °C)
X-1 <sup>1</sup>	66	54,000	11,300	62	
X-1A <sup>1</sup>	69	54,500	11,400	62	
X-1B <sup>1</sup>	72	57,800	13,500	60	
X-1C <sup>1</sup>	131	69,800	45,000	42	
X-1 <sup>2</sup>	161	75,400	45,900	39	25.0
X-1A <sup>2</sup>	159	77,600	50,000	38	24.2
X-1B <sup>2</sup>	161	78,700	53,600	37	24.3
X-1C <sup>2</sup>	173	79,300	61,600	34	22.9

\* 0.2% offset method.

† All specimens were 0.058" thick.

<sup>1</sup> Cold-rolled specimens heated 1.5 hours at 750 °C, water-quenched, and aged 3 hours at 400 °C.

<sup>2</sup> Cold-rolled specimens annealed for 6 hours at 400 °C.

The data of Table 20 show that neither the X-1 alloy containing no silver, nor the X-1A and X-1B alloys containing 0.1 and 1.0 per cent of silver, respectively, precipitation-harden to any significant extent. However, the X-1C alloy containing 3.65 per cent of silver showed a marked response to the precipitation treatment, the increase in hardness and yield strength being accompanied by very little decrease in ductility. It will be noted, in comparing the hardness data on the specimens cold-rolled and annealed at 400 °C with the hardness of the alloys as cast (Table 19), that the specimens were still in the work-hardened state. Subsequent annealing studies showed that although these alloys lost most of the hardness produced by cold work after heating for 3 hours at 400 °C, annealing at 600 °C for 6 hours was insufficient to reduce the hardness to the values of the as-cast metal. This statement applies to number 18-gauge sheet cooled in air from the annealing temperature.

It was also found that about 1 per cent of silver raised the annealing temperature slightly, and the castability of the alloy was improved by silver in the range investigated. The corrosion resistance of the alloy was apparently unaffected by the addition of silver.

It is conceivable that an alloy of this type containing enough silver to impart precipitation-hardening characteristics would find application in welded assemblies requiring higher strength than can be obtained in annealed copper-silicon-manganese sheet. The heat of welding would cause the loss of much of the greater strength that might be imparted by cold-rolling the sheet before fabrication, but the silver-containing alloy could subsequently be heat-treated to a high yield strength.

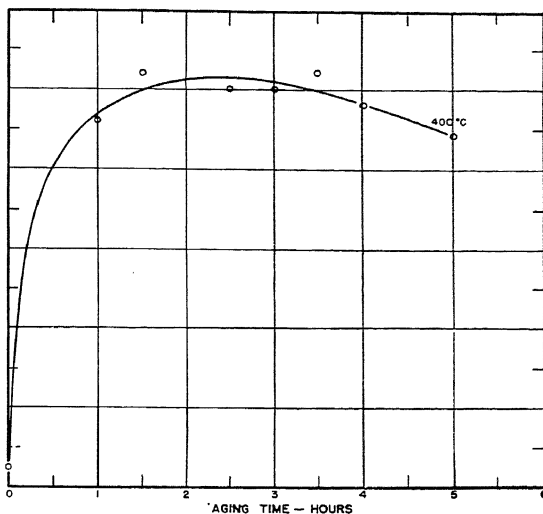


FIGURE 6. Response to heat treatment of a low-tin bronze containing silver.

Alloy C-5C: 4.31% tin, 4.63% silver, remainder copper. Cold-rolled  $\frac{1}{8}$ " plate, homogenized 49 hours at 700 °C, quenched in water, and aged as indicated.

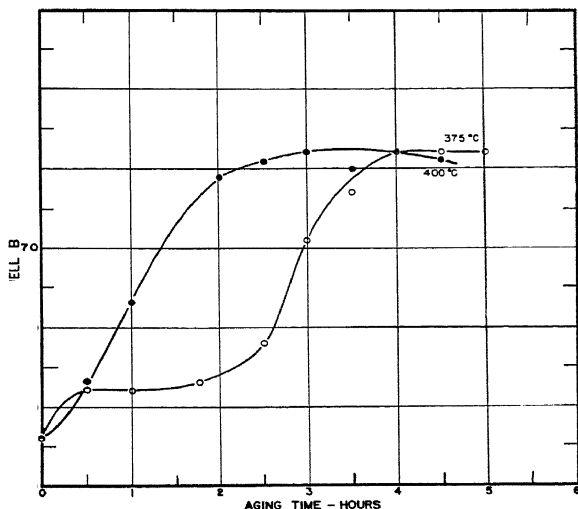


FIGURE 7. Response to heat treatment of a high-tin bronze containing silver.

Alloy C-9C: 8.66% tin, 5.83% silver, remainder copper. Cold-rolled  $\frac{1}{8}$ " plate, homogenized 49 hours at 720 °C, quenched in water, and aged as indicated.

### 10. Copper-tin Alloys (Bronzes)

The effect of adding silver to three classes of tin bronze has been studied. Three series of alloys were studied, containing respectively about 5 per cent tin (C-5 series), about 10 per cent tin (C-9 series), and about

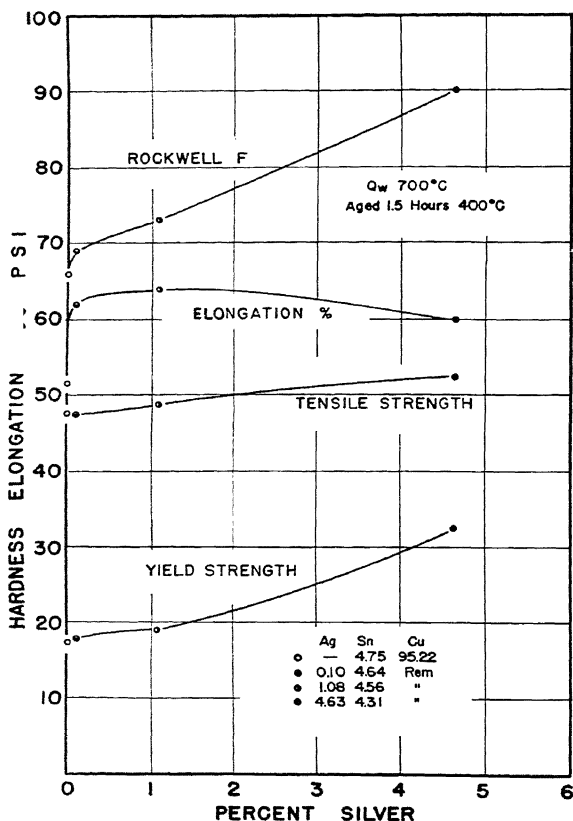


FIGURE 8. Effect of silver on physical properties of low-tin bronze.

20 per cent tin (C-8 series) (Table 1). Alloys marked CC were from check heats prepared somewhat later than those of the main series. All melts were deoxidized with phosphor-copper, care being taken to keep the residual phosphorus below 0.1 per cent.

Figures 6 and 7 show the response to heat-treatment, observed by B. S. Old, of alloys C-5C and C-9C respectively. Neither the silver-free

controls nor the C-5B and C-9B showed any evidence of precipitation-hardening.

The physical properties of wrought and heat-treated alloys representing a series of low-tin bronzes containing silver ranging from 0.1 to 4.63 per cent are summarized graphically in Figure 8. Companion data on

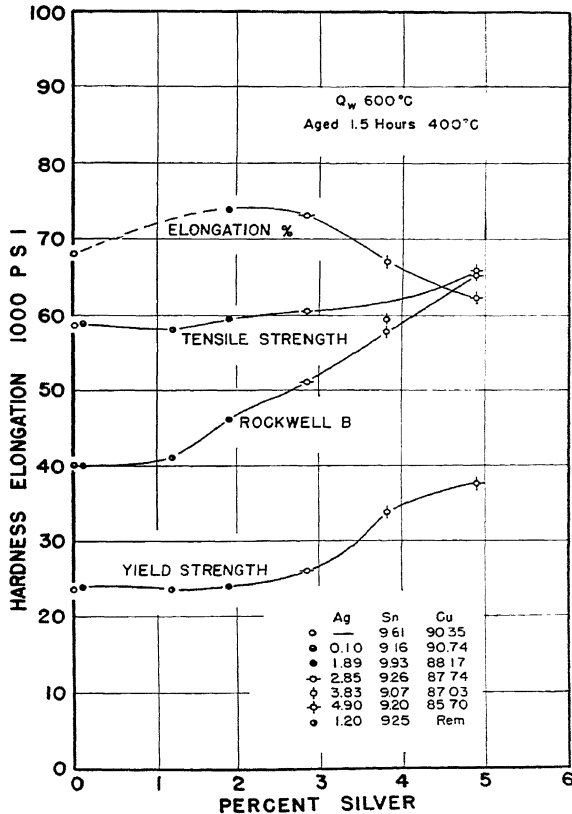


FIGURE 9. Effect of silver on physical properties of high-tin bronze.

high-tin bronzes with silver ranging from 0.1 to 4.9 per cent are summarized graphically in Figure 9. These figures show the effect of silver on the properties of these bronzes.

The results of some tests carried out to demonstrate the effect of cold work on a high-tin bronze, with and without silver additions, are summarized in Table 21. The aging temperature (400 °C) selected was sub-

Table 21.—Influence of Cold Work, and Cold Work Before Aging, on Physical Properties of Copper-Tin-Silver Alloys.

Alloy	Vickers Rolled <sup>1</sup>	Number Aged <sup>2</sup>	Tensile Strength p. s. i.		Yield Strength* p. s. i.		Elongation (% in 2")	
			Rolled <sup>1</sup>	Aged <sup>2</sup>	Rolled <sup>1</sup>	Aged <sup>2</sup>	Rolled <sup>1</sup>	Aged <sup>2</sup>
C-0	176	125	78,100	66,500	61,100	36,100	48	54
C-1	170	147	75,900	72,600	57,100	42,800	50	50
C-3	161	155	75,400	72,800	60,000	57,300	49	45
C-4	183	162	84,000	79,500	69,500	57,000	41	43

<sup>1</sup> Specimens cold-rolled 20% to 0.10" thick after 600 °C annealing.

<sup>2</sup> Specimens water-quenched after 1 hour at 600 °C, then cold-rolled 20% to .10" and aged 1½ hours at 400 °C.

\* 0.2% offset method.

sequently found to be high enough to produce some softening in cold-worked material of similar composition. Hence the observed physical properties were influenced by the tendency of the cold-worked material to lose its strain-hardened characteristics at the same time that precipitation-hardening setting in at 400 °C tended to raise the physical properties.

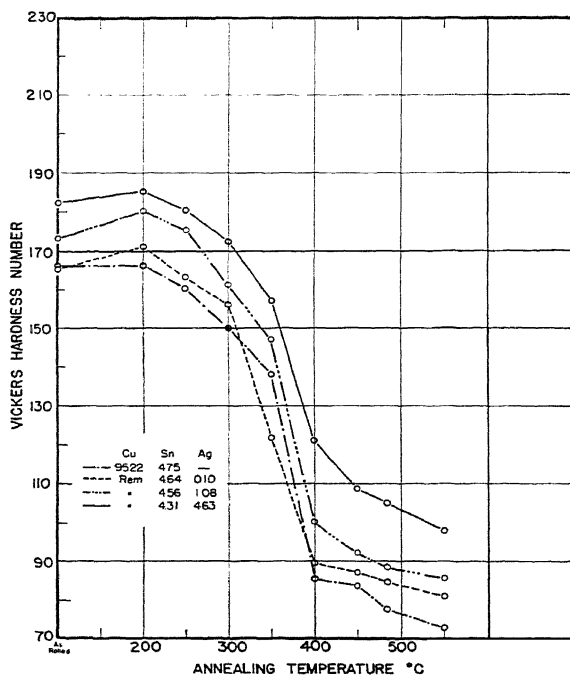


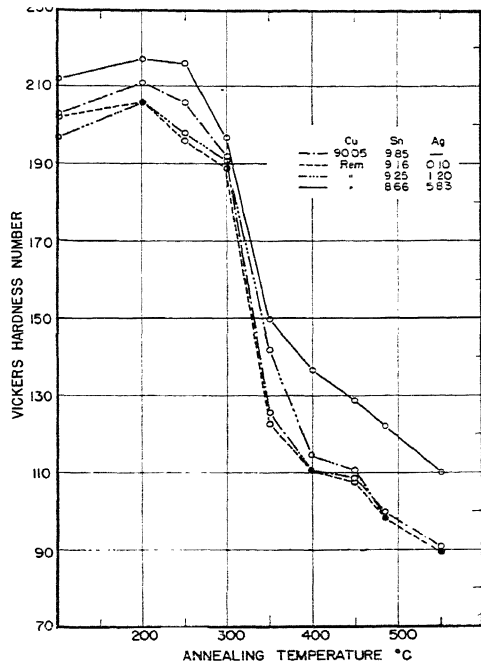
FIGURE 10. Effect of silver on softening temperature of copper-tin alloys.

Specimens cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge. Annealing time, 5.5 hours.

FIGURE 11.

Effect of silver on softening temperature of copper-tin alloys.

Specimens cold-rolled from No. 15 B. & S. to No. 18 B. & S. gauge. Annealing time, 5.5 hours.



The effect of silver on the temperature required for annealing cold-worked low-tin bronze is shown in Figure 10, and in Figure 11 for a high-tin bronze.

Silver, in sufficient percentage, restrained grain-growth upon annealing in both the low- and high-tin bronzes. Data on the grain size of the high-tin alloys after annealing, as determined by the A.S.T.M. method at 75 $\times$  magnification, are given in Table 22. It was also observed that

Table 22.—Effect of Silver on Grain Growth in Annealed Bronzes.

Alloy	% Ag	Temp. (°C)	Grain Size	Temp. (°C)	Grain Size
C-0	0.0	600	.075	700	.180
C-1	1.89	600	.090	700	.200
C-6	2.85	600	.075	700	.175
C-3	3.83	600	.055	700	.120
C-4	4.9	600	.035	700	.080

silver decreased the size of the primary dendrites of all the sand-cast bronzes, the effect being most pronounced in the 10-per cent tin bronze, and least in the 20-per cent tin bronze. The effect was greatest with the highest percentages of silver. With the exception of the 5-per cent tin

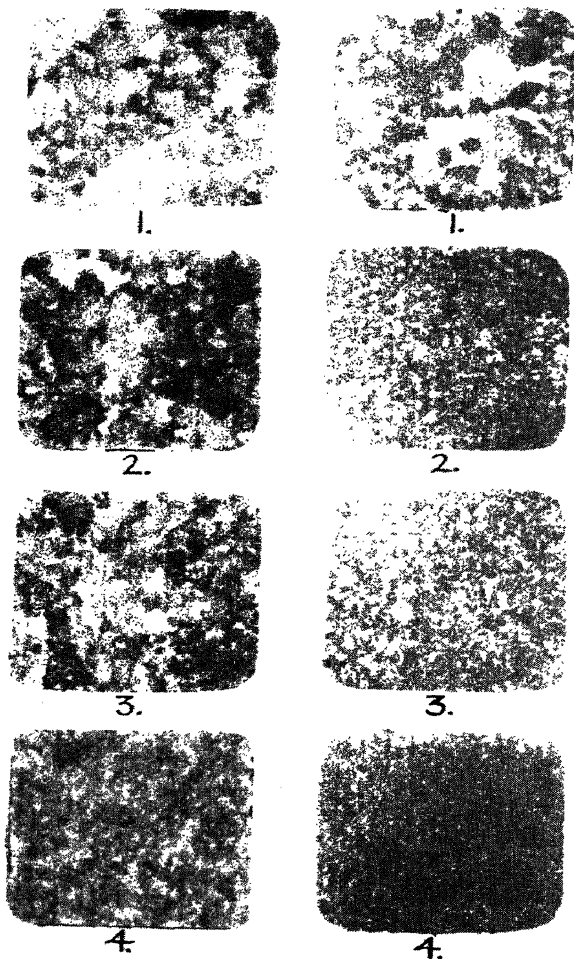


FIGURE 12. Grain refinement in sand-cast tin bronzes produced by silver.

Left side:  
 1. 9.85% tin, 0.0% silver.  
 2. 9.16% tin, 0.1% silver.  
 3. 9.25% tin, 1.20% silver.  
 4. 8.66% tin, 5.83% silver.

Right side:  
 1. 19.91% tin, 0.0% silver.  
 2. 19.69% tin, 0.1% silver.  
 3. 18.81% tin, 1.12% silver.  
 4. 18.36% tin, 4.18% silver.

Magnification  $\times 3$ ; etchant  $\text{FeCl}_3$ ; 1120 °C, pouring temperature.

bronze, 0.1 per cent of silver was enough to have significant effect of this nature; in this instance about 1 per cent of silver was required for grain refinement. These observations were made on similar specimens cut from castability test "stars" poured at the same casting temperature in a given series. Figure 12 illustrates the grain-refining effect of silver in the 10- and 20-per cent tin bronzes.

Table 23.—Physical Properties of Sand-Cast Copper-Tin-Silver Alloys.

Alloy	Rockwell B Number	—Hardness—		Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elonga- tion (% in 2")	Yield Point in Compression .0005" Set
		Brinell Number	Brinell Number				
C-0	40†	56†	84†	32,500	17,300	19	15,000
C-1	—	64†	86†	35,000	19,000	16	—
C-6	38‡	63†	88†	45,000	20,500	30	14,000
C-3	—	—	77†	37,900	18,200	21	—
C-4	44‡	67†	89†	33,400	19,000	10	23,500
CC-8	83‡	—	129†	29,300	29,300	0.0	24,300
CC-9	82‡	—	114†	25,000	25,000	0.0	17,500
CC-10	74‡	—	109†	29,500	29,500	0.0	19,000

\* 0.2% offset method.

† Measurements taken on surface of chill-cast test slab.

‡ Measurements taken on machined cross-section, and do not represent surface hardness.

The properties of a group of sand-cast 10- and 20-per cent tin bronzes are summarized in Table 23. The effect of heat-treatment on the properties of these alloys is indicated by the data of Table 24.

Table 24.—Physical Properties of Heat-treated Sand-Cast Copper-Tin-Silver Alloys.

Alloy	—Hardness—		Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elonga- tion (% in 2")	Yield Point in compression .0005" set p. s. i.	Remarks
	Rockwell Number	Brinell Number					
C-0	25B	—	35,000	17,800	30	14,700	Note 1
CC-0	59F	49	31,500	17,600	16	9,200	Note 2
CC-1	59F	53	21,900	18,000	2	10,450	Note 2
C-6	53B	—	27,000	27,000	0	18,400	Notes 1, 3
CC-2	68F	63	28,000	25,100	1.2	14,700	Note 2
CC-3	78F	70	28,900	27,900	0.5	20,200	Note 2
C-4	58B	—	—	—	—	30,500	Note 1
CC-8	86B†	147†	22,200	22,200	0.0	26,300	Note 2
CC-9	75B†	125†	24,300	24,300	0.0	23,100	Note 2
CC-10	74B†	120†	25,900	25,900	0.0	29,300	Note 2

Note 1. Specimens homogenized 45 hours at 700 °C, quenched in water, and aged 2½ hours at 400 °C.

Note 2. Specimens homogenized 48 hours at 600 °C, quenched in water, and aged 2½ hours at 400 °C.

Note 3. 700 °C homogenization temperature apparently excessive, producing intergranular weakness.

\* 0.2% offset method.

† Measurements taken on machined cross-section, and do not represent surface hardness.



It was noted that the hardness and response to heat-treatment of bronzes containing about 20 per cent of tin were markedly affected by the initial structure of the cast metal. The difference in hardness of the alloys determined at the surface and on a cross-section near the interior of the cast slab is brought out by the data of Table 25. This difference

Table 25.—Difference in Properties of Surface and Interior Portions of Sand-Cast Copper-Tin-Silver Alloys.

Treatment	Alloy	—Hardness at Center—		—Hardness at Surface—	
		Rockwell Number	Brinell Number	Rockwell Number	Brinell Number
As cast	CC-8	81B	124	95B	175
	CC-9	72B	102	95B	171
	CC-10	66B	107	95B	166
Homogenized (heated 48 hours at 600 °C and quenched in water)	CC-8	77B	97	85B	147
	CC-9	64B	82	88B	152
	CC-10	64B	89	86B	139
Aged (reheated after homogenization to 400 °C for 2½ hours)	CC-8	87B	147	85G	232
	CC-9	87B	109	85G	219
	CC-10	83B	147	85G	219

is undoubtedly associated with the finer structure of the alloy close to the surface, and a chill-zone, following the periphery of the cross-section, could be readily discerned. The response of the chill-zone material to heat-treatment is notable, the very high hardness being especially interesting. Chemical analysis showed that the difference in composition between the surface and the interior was too small to account for the observed differences in hardness.

Table 26—Resistivity of Copper-Tin-Silver Alloys.

Alloy	Condition	Resistivity microhm-cm (20 °C)
C-5	} Annealed sheet, furnace-cooled from 400 °C.	9.5
C-5A		10.7
C-5B		11.4
C-5C		11.8
C-0	} Sheet, cold-rolled 20% and then heated 1½ hours at 400 °C.	12.8
C-1		16.5
C-6		16.0
C-3		15.7
C-4		12.9
CC-8	} Sand cast	32.1
CC-9		32.3
CC-10		34.2
CC-8	} Sand cast, homogenized 48 hours at 600 °C, quenched in water, reheated 2½ hours at 400 °C, and cooled in furnace.	31.4
CC-9		31.5
CC-10		34.8

Table 26 summarizes data obtained on the resistivity of the tin bronze alloys.

A review of the data obtained on the copper-tin-silver alloys leads to the following conclusions:

(1) The presence of about 3 per cent of silver in wrought alloys of copper with from 5 to 10 per cent of tin renders them susceptible to precipitation-hardening.

(2) Heat-treated bronzes of this type are characterized by marked increase in yield strength with no significant decrease in ductility, electrical conductivity, or resistance to corrosion.

(3) Moderate cold-rolling produced physical properties superior to those obtained by heat-treating 10-per cent tin bronzes containing economically reasonable proportions of silver.

(4) Cast alloys of copper with 10 per cent of tin containing 3 to 5 per cent of silver respond mildly to a precipitation-hardening treatment, but the improvement is not sufficient to justify the cost of the silver required.

(5) Silver produces grain refinement in cast bronzes and restrains grain growth in wrought bronzes.

(6) The addition of silver to bronzes containing 5 to 10 per cent of tin increases their general hardness and annealing temperature, these effects being particularly noticeable with 1 per cent or more of silver, and for annealing periods of short duration.

## 11. Copper-zinc Alloys (Brasses)

The effect of silver on some properties of brasses containing from 10 to 40 per cent of zinc has been studied. The compositions of the alloys

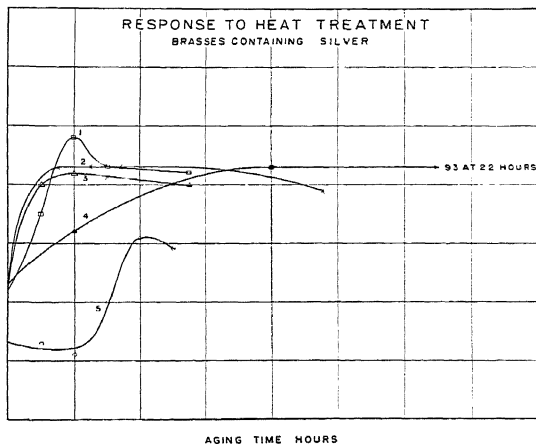


FIGURE 13. Response to heat treatment of brasses containing silver.

Curve 1. Alloy B-6B: Quenched from 820 °C, aged at 250 °C. Rockwell B hardness readings.  
 Curve 2. Alloy B-6: Quenched from 820 °C, aged at 250 °C. Rockwell B hardness readings.  
 Curve 3. Alloy BB-9C: Quenched from 720 °C, aged at 400 °C. Rockwell F hardness readings.  
 Curve 4. Alloy BB-9C: Quenched from 720 °C, aged at 350 °C. Rockwell F hardness readings.  
 Curve 5. Alloy BB-8C: Quenched from 870 °C, aged at 450 °C. Rockwell F hardness readings.

investigated are given in Table 1. Aging studies by B. S. Old showed that, with the exception of the 60-40 brass (B-6), none of the brasses without silver responded to precipitation-hardening treatments, and that the addition of about 1 per cent of silver to these alloys was insufficient to make any change in their response. The B-9C alloy was precipitation-hardenable, as were also the BB-8C, BB-7C, B-6A and B-6B alloys. Probably the response noted in the B-6A and B-6B alloys can be attributed to the transformation of the  $\beta$ -phase of the 60-40 brass. Figure 13 shows the response of these brasses to precipitation-hardening heat treatment.

Data on the physical properties of the brasses investigated are summarized in Table 27. Annealing data for these alloys, when plotted,

Table 27.—Physical Properties of Copper-Zinc-Silver Alloys.

Alloy	Hardness Rockwell Number	Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elongation (% in 2")	Resistivity microhm-cm (20 °C)
B-9	60F	39,300	12,700	41.0	4.1
B-9A	59F	40,800	12,900	45.0	4.1
B-9B	66F	45,700	16,800	42.0	4.1
B-9C	86F	51,300	32,400	41.5	4.0
BB-8	62F	46,000	14,700	50.5	5.6
BB-8A	67F	47,900	16,700	52.0	5.6
BB-8B	68F	49,000	18,100	54.5	5.6
BB-8C	78F	53,600	24,200	52.0	5.7
BB-7	62F	50,000	15,500	58.0	6.2
BB-7A	63F	49,700	15,200	56.5	6.4
BB-7B	66F	51,000	16,200	57.0	6.3
BB-7C	79F	57,900	23,500	57.5	6.5
B-6	83B	69,500	42,700	7.5	6.6
B-6A	83B	70,800	42,500	15.3	6.6
B-6B	77B	73,200	39,600	21.0	7.0

Alloy Series B9, BB8, and BB7 were cold-rolled and annealed at 600 °C for 15 min.

Alloy Series B6 was cold-rolled, given a solution heat treatment by heating to 820 °C for 20 min. and water-quenching; then aged 2½ hours at 250 °C.

Resistivity measurements taken on specimens heated 6 hours at 400 °C.

\* 0.2% offset method.

resembled the curves shown in Figure 4, in that the addition of about 0.1 per cent of silver had little effect, whereas 1 per cent or more of silver raised the general hardness and annealing temperature. The influence of silver on the annealing characteristics was most pronounced in the alloys of lowest zinc content. With 30 per cent of zinc in the alloy, 1 per cent of silver was only approximately as effective as 0.1 per cent in the 10-per cent zinc alloys. Table 28 summarizes data on the hardness of the alloys as chill-cast, wrought and annealed, and as cold-rolled from number 15 to number 18 B & S gauge.

No significant effect of silver was detected in either the castability or corrosion tests. However, it was observed that pickling, or anodic corrosion, of the brasses containing the highest percentages of silver

Table 28.—Hardness of Copper-Zinc-Silver Alloys.

Alloy	Chill cast		Vickers Number	
	Brinell Number	Rockwell E Number	Annealed <sup>1</sup>	Cold-rolled
B-9	45		55	126
B-9A	42		56	125
B-9B	49		62	133
B-9C	67		93	147
BB-8	48	50	66	157
BB-8A	48	52	70	157
BB-8B	49	53	73	159
BB-8C	59	72	92	167
BB-7	43	47	66	145
BB-7A	44	47	66	147
BB-7B	49	56	68	154
BB-7C	69	74	88	169
B-6	75	84	81	156
B-6A	72	83	77	157
B-6B	72	82	76	157

<sup>1</sup> One hour at 600 °C (No. 18 B. & S. gauge sheet).<sup>2</sup> From No. 15 B. & S. to No. 18 B. & S. gauge.

resulted in the formation of a silver film on the surface of the alloy. It is claimed (U. S. Patent 2,188,681) that a fractional percentage of silver prevents dezincification of brass. There may be some connection between these observations.

It was found that silver additions to the brasses produced a reduction in the grain size of sand-cast material, the effect increasing with increasing proportions of silver. In the case of the 60-40 brass, the addition of 1.1 per cent of silver also affected the microstructure, seemingly producing a dendritic structure instead of the acicular structure of the alpha-silver transformation product in a beta-matrix.

Except for the grain-refining effect, the elevation of the annealing temperature, and the high yield strength produced by silver, the effect of silver on the physical properties of brasses does not appear significant. While there may be special applications where these improvements warrant the cost of the silver additions, the effect of silver on dezincification is of much greater commercial interest. The importance of copper-zinc-silver alloys, containing higher percentages of silver than were included in this investigation, for use as brazing alloys is to be noted. This matter is taken up in Chapter 7.

## 12. Lead-antimony Alloys

A group of lead alloys containing about 12 per cent of antimony was prepared, with silver ranging from 0.1 to 4.79 per cent. The purpose in studying these alloys was to note the effect of silver on the castability of a 12-per cent antimony alloy used for storage battery grids. Table 29 summarizes the data obtained on the hardness and castability of these alloys. The hardness was determined on chill-cast specimens; the castability was measured by the extent to which the alloys filled the castabil-

ity mold (see Figure 1). The data indicate that the addition of up to 1 per cent silver may have slightly improved the castability, but the differences in any case were not large. Furthermore, there is a question as to what significance should be attached to data on the sand-cast specimens, inasmuch as commercial grid alloys are always chill-cast.

Table 29.—Hardness and Castability of Lead-Antimony-Silver Alloys.

Alloy	Chill-cast Hardness Brinell Number	Castability	
		Pouring Temperature (°C)	Per Cent Rating
U	16	495	92
U-A	17	495	94
U-B	15	495	95
U-C	15	495	90

A comprehensive study of the effect of from 0.05 to 0.15 per cent of silver on the physical, electrochemical, and corrosion properties of storage battery grid alloys containing from 4 to 12 per cent of antimony has been made by Dornblatt (Dissertation submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree, Columbia University, 1940, on "The effect of silver on the properties and performance of antimonial-lead storage battery grids"). Silver was found to greatly reduce anodic corrosion of the antimonial-lead alloys in sulfuric acid, and to impart better physical properties to the heat-treated alloys.

Table 30.—Composition and Shear Strength of Lead-Tin-Silver Solders.

Nominal Composition (%)			Shear Strength p. s. i.
Pb	Sn	Ag	
95	0.5	4.5	2700
95	1.5	3.5	2890
95	2.5	2.5	2960
95	3.5	1.5	3250
95	4.5	0.5	3290
95	5.0	0.0	3280
90	5.5	4.5	3150
90	6.5	3.5	3110
90	7.5	2.5	3980
90	8.5	1.5	3890
90	9.5	0.5	3900
90	10.0	0.0	4100
85	10.5	4.5	3970
85	11.5	3.5	4050
85	12.5	2.5	4220
85	13.5	1.5	4200
85	14.5	0.5	4490
85	15.0	0.0	4400
80	15.5	4.5	4560
80	16.5	3.5	4530
80	17.5	2.5	4730
80	18.5	1.5	4630
80	19.5	0.5	4880
80	20.0	0.0	4510

### 13. Lead-tin Alloys

Tests were carried out on lead-tin solders containing 0.0 to 4.5 per cent of silver and up to 20 per cent of tin. The strength of soldered joints, tested in shear at room temperature, was determined. The results are given in Table 30. The addition of 0.5 per cent of silver to the solders containing 15 per cent and 20 per cent of tin improved the shear strength somewhat. The addition of more than 0.5 per cent of silver did not give greater improvement than could be obtained by equivalent amounts of tin. Additional data on lead-silver and lead-tin solders are given in Chapter 3, where the advantage of the lead-silver solders for service at elevated temperature is discussed.

Additional work may be warranted on solders of higher tin content containing small proportions of silver. Other investigators have reported improved physical properties with such lead-tin solders containing a very small percentage of silver.

### 14. Magnesium-tin Alloys

In view of work at the National Physical Laboratory in England showing that silver imparts superior physical properties to certain magnesium-base light alloys, it was decided to investigate the effect of silver

Table 31.—Physical Properties of Magnesium-Tin-Silver Alloys.

Alloy†	Hardness Rockwell F Number	Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elongation (% in 2")	Reduction Area (%)	Charpy Impact (ft/lbs)
<i>As Extruded<sup>1</sup></i>						
11919	—	35,100	23,700	12.6	12.0	2.66
11920	—	35,500	24,300	17.0	11.7	—
11921	—	42,300	31,600	10.4	5.4	2.53
11922	—	37,000	26,600	4.5	8.0	—
11923	—	35,000	23,600	11.3	12.0	—
11924	—	35,400	25,100	12.6	4.3	—
<i>As Quenched<sup>2</sup></i>						
11919	35	32,600	22,000	11.9	8.7	—
11920	38	31,900	21,850	8.0	—	—
11921	60	40,600	28,120	11.4	4.15	—
11922	33	36,440	22,800	8.5	2.3	—
11923	23	25,200	22,700	—	—	—
11924	25	26,950	23,200	—	—	—
<i>As Aged at 302 °C</i>						
11919	64	43,220	31,000	3.5	3.	1.0
11920	72	31,800	22,900	4.4	0.89	—
11921	58	46,400	38,000	1.5	0.78	1.0
11922	40	38,400	29,000	1.0	0.89	—
11923	53	32,000	26,100	3.0	0.99	—
11924	55	31,800	27,100	3.5	—	—

<sup>1</sup> Alloys were extruded at 370 °C at 6 to 8 feet per minute.

<sup>2</sup> Alloy No. 11919 was homogenized for one hour at 535 °C and water-quenched. All others were homogenized for two hours at 520 °C and water-quenched.

\* 0.2% offset method.

† Standard tensile bars machined to 0.505" diameter.

on a group of magnesium-rich alloys of several different types. The compositions of some magnesium-tin alloys investigated are given in Table 1. The M-series of alloys was prepared at the National Bureau of Standards and used in preliminary studies. Through the courtesy of the Dow Chemical Company, another group of alloys was prepared under commercial conditions and the properties of these alloys investigated both by B. S. Old at the Massachusetts Institute of Technology and the Project staff at the National Bureau of Standards. Table 31 summarizes the results of tests made at the Institute which should be compared with the data of Table 32, summarizing the results of tests made by the Project. The superior tensile strength and ductility noticeable in Table 32, particularly in the case of the alloys 11923 and 11924, is probably a

Table 32.—Physical Properties of Magnesium-Zinc-Silver Alloys.

Alloy†	Hardness		Tensile Strength p. s. i.	Yield Strength* p. s. i.	Elongation (% in 2")
	Brinell Number	Rockwell F Number			
<i>As Extruded</i> <sup>1</sup>					
11920	47	49	35,800	25,400	15.0
11921	53	62	42,750	31,400	14.5
11923	45	45	35,300	24,900	16.0
11924	47	47	35,600	24,600	15.5
<i>As Quenched</i> <sup>2</sup>					
11920‡	41	33	31,650	23,350	2.5
11921	48	57	41,200	29,200	15.5
11923	43	39	34,550	23,000	14.0
11924	44	41	34,350	23,300	15.0
<i>As Aged</i> <sup>3</sup>					
11920‡	48	54	32,900	25,650	2.0
11921	58	67	44,900	31,550	9.0
11923	50	54	39,050	26,100	7.5
11924	49	56	38,900	25,600	7.0

<sup>1</sup> Alloys were extruded at 370 °C at 6 to 8 feet per minute.

<sup>2</sup> Alloys homogenized 1 hour at 500 °C and water-quenched.

<sup>3</sup> Alloys aged 40 hours at 300 °C.

\* 0.2% offset method.

† Standard tensile bars machined to 0.505" diameter.

‡ Specimen heated beyond critical range; outer shell showed grain growth.

consequence of the lower homogenizing temperature used at the Bureau. It was found that temperatures above 500 °C promoted a serious coarsening of the grain structure, while at 520 °C the danger of spontaneous combustion of the alloys was appreciable.

Corrosion tests in 3-per cent sodium chloride solution showed that the tendency of silver to accelerate the corrosion of the magnesium-tin alloys was substantially reduced by the presence in the alloy of about 0.5 per cent of manganese, except in the case of the alloy which also contained 3 per cent of aluminum. The corrosion data summarized in Table 33

Table 33.—Corrosion\* of Magnesium-Tin-Silver Alloys.

Alloy	(mg/cm <sup>2</sup> /day)		
	As Extruded <sup>1</sup>	As Quenched <sup>2</sup>	As Aged <sup>3</sup>
11919	3.05	1.61	2.21
11920	1.10	0.89	1.45
11921	3.32	3.13	4.42
11922	1.33	0.63	0.66
11923	1.34	1.05	1.22
11924	1.37	1.50	1.08

\* Alternate immersion in 3% NaCl at 95 °F for 1 month.

<sup>1</sup> Alloys were extruded at 370 °C at 6 to 8 feet per minute.

<sup>2</sup> Alloy No. 11919 was homogenized for one hour at 535 °C and water-quenched. All others were homogenized for two hours at 520 °C and water-quenched.

<sup>3</sup> Alloys aged at 302 °C.

illustrate this point. The least corrosion was observed in the case of the silver-free alloy. The corrosion of the other alloys was about the same as that of some commercial magnesium alloys.

It was observed that the ingots containing silver were finer-grained than those of similar composition not containing silver.

The addition of 1.3 to 2.5 per cent of silver did not produce any striking improvement in physical properties of magnesium alloys containing about 6 per cent of tin. However, the properties of alloy 11921, containing 3 per cent of aluminum in addition to the tin and silver, were found to be excellent. It is known that aluminum is an effective strengthening element, and the data do not permit evaluation of the extent to which silver contributed to the unusually high physical properties of this light-weight alloy.

## 15. Magnesium-zinc Alloys

Limited experiments were carried out on the magnesium-zinc alloys prepared at the National Bureau of Standards having the compositions given in Table 1. Table 34 lists some data on hardness of these alloys, and Table 35 gives some results of heat-treating studies.

Table 34.—Hardness of Chill-cast Magnesium-Zinc-Silver Alloys.

Alloy	Brinell Number	Rockwell E Number
L-1	41	47
L-1A	48	58
L-1B	49	60
L-1C	54	69
L-2	51	66
L-2A	53	70
L-2B	65	84
L-2C	86	95

Corrosion studies showed that the addition of silver to the magnesium-zinc alloys accelerated their rate of corrosion. Presumably the rate of attack could be reduced by manganese additions, for it is known that 0.5



Table 35.—Aging Properties of Magnesium-Zinc-Silver Alloys.<sup>1</sup>

Alloy	Condition	—Hardness (Rockwell F No.)—		Aging Time (hours)
		As Quenched	Aged	
L-1	Wrought <sup>2</sup>	49	71	1.75
L-1A	Wrought <sup>2</sup>	57	76	1.75
L-1B	Wrought <sup>2</sup>	60	66	2.25
L-1C	Wrought <sup>2</sup>	66	70	1.75
L-2	Wrought <sup>2</sup>	59	80	1.75
L-2A	Cast	64	80	1.75
L-2B	Cast	76	87	1.75
L-2C	Cast	88	93	1.75

<sup>1</sup> Alloys were homogenized 25 hours at 300 °C in a CO<sub>2</sub> atmosphere, quenched in water and aged at 193 °C in a carbitol bath.

<sup>2</sup> Hot-forged at 300 °C.

per cent of manganese has a very beneficial effect on the corrosion-resistance of magnesium-rich alloys.

The data for the L-1 series of alloys show that silver hardened the 7-per cent zinc alloy quite substantially, although more than 1 per cent of silver did not improve the aging properties. No conclusion regarding the effect of silver in the L-2 series of alloys can be drawn, because of the large variation in zinc content.

#### 16. Silver-aluminum-titanium Alloys

The effect of titanium in refining the grain of aluminum alloys prompted a study of the properties of silver-aluminum alloys containing

Table 36.—Hardness of Chill-cast Silver-Aluminum-Titanium Alloys.

Alloy	Brinell Number	Rockwell B Number	Remarks
NT-1	38	36	Much segregation.
NT-2	93	96	Large differences
NT-3	77(?)	98	in hardness from top
NT-4	113	96	to bottom of ingots.

titanium. The alloys investigated were of the compositions given in Table 1. The hardness of the chill-cast alloys is given in Table 36, and the aging properties of the wrought alloys are summarized in Table 37.

Table 37.—Aging Properties of Wrought Silver-Aluminum-Titanium Alloys.

Alloy	—Hardness (Rockwell F No.)—	
	As Quenched	After Aging
NT-1	1	1
NT-2	77	117 <sup>2</sup>
NT-3	59	77 <sup>2</sup>
NT-4	1	1

<sup>1</sup> No aging.

<sup>2</sup> Aged for 8 hours at 245 °C.

These data should be compared with those reported in Table 2 of Chapter 3 on binary silver-aluminum alloys of similar composition.

The 92-8 silver-aluminum alloy was not workable, but the NT-3 alloy of almost identical composition, except for the presence of 0.1 per cent of titanium, could be rolled cold. The alloys containing titanium had a fine grain structure. The hardness of the NT-2 alloy after aging is especially noteworthy. It would be quite interesting to know the physical properties of alloys such as these which contain 6 to 8 per cent of aluminum and which can be wrought and heat-treated to a hardness comparable with, or higher than, that of other non-ferrous alloys and low-carbon steel.

De Marchi found that the unheat-treated NT-1 alloy had a very low corrosion loss, the NT-2 was appreciably attacked, whereas the NT-3 and NT-4 continued to corrode even after the test had been discontinued and the specimens dried. The reflectivity factor for NT-1 alloy was found to be 0.85.

### 17. Silver-copper-silicon Alloys

In Chapter 3, reference was made to the properties of copper-silver alloys containing 7.5 per cent of copper (Table 12), and to the properties of silicon-silver alloys containing small percentages of silicon (Table

Table 38—Hardness of Chill-cast Silver-Copper-Silicon Alloys.

Alloy	Brinell Number	Rockwell E Number
V-1	48	55
V-2	53	61
V-3	65	74
V-4	77	84
V-5	89	91

27 and Figure 37). It was decided to study the properties of silver-rich alloys containing both copper and silicon, which might be expected to contain copper silicide. The V-series of alloys, of compositions listed in Table 1, was therefore prepared. The hardness of the chill-cast alloys is given in Table 38, and data on their aging properties in Table 39.

Table 39.—Aging Properties of Silver-Copper-Silicon Alloys.<sup>1</sup>

Alloy	Condition	—Hardness (Rockwell F No.)—		Aging Time (hours)
		As Quenched	Aged	
V-1	Wrought	25	52	1.5
V-2	Wrought	38	56	1.0
V-3	Wrought	52	83	2.0
V-4	Wrought	60	80	1.5
V-5	Cast	57	97	2.5

<sup>1</sup> Alloys were homogenized 13 hours at 750 °C, water-quenched and aged at 250 °C

With the exception of the alloy V-5, none of these alloys aged to the same degree as did the 7.5-per cent copper alloy, which attained a hardness of 99 Rockwell F. The data of Table 39 are not final, since the alloys were not as thoroughly worked as the 7.5-per cent copper alloy,

nor is it certain that the aging treatment was the one to give the optimum improvement in hardness.

The optical reflectivity of the V-1, V-2, V-3 and V-4 alloys was measured, and reflectivity factors were obtained for these alloys, in order, 0.87, 0.81, 0.66 and 0.73.

According to de Marchi's tests, the corrosion resistance of the silver alloys containing copper and silicon was not as high as that of fine silver.

#### 18. Silver-magnesium-silicon Alloys

Magnesium and silicon were added to silver with the idea of observing whether or not the aging properties found in the silicon-silver alloys would be intensified by the formation of magnesium-silicide. The data obtained were given in Table 28 of Chapter 3.

#### 19. Silver-manganese-silicon Alloys

The possibility of forming manganese-silicide in silver-rich alloys containing a substantial percentage of manganese was considered, and the alloys designated WX in Table 1 were prepared for study. The data obtained have been summarized in Table 25 of Chapter 3.

#### 20. Silver-silicon-nickel Alloys

The possibility of forming nickel silicide in silver-rich alloys was considered, and the alloys designated S-X and SS-B in Table 1 were prepared for study.

These alloys have been discussed, together with other alloys of silicon and silver, in Chapter 3.

### III. RECAPITULATION

#### 1. General

The development of a new alloy that can be placed on the market for industrial applications is, inherently, a very laborious and involved undertaking. Exhaustive investigation is necessary to insure that the properties are commercially reproducible, that they are so superior or unusual that the new alloy can compete with established alloys, and that the alloy is free from peculiarities which, if revealed only in service, may cause user and producer much grief and expense. The Project has not developed any new alloy which it advocates for commercial production, but it has endeavored to point out some useful properties of certain alloys, and, by its exploratory investigations, to suggest further investigation of alloys which appear to have some interesting properties, as well as show cause why other alloys do not warrant further investigation.

#### 2. Effect of Small Additions of Silver

It is of interest to review some of the effects which a small proportion of silver produces in alloys containing silver as a minor constituent. These are as follows:

*Annealing temperature.* Silver, even in very small proportion, raises the annealing temperature of copper and the alpha-phase alloys rich in copper or nickel. The influence of silver is most pronounced in the binary alloys, and seems to be weakened as the proportion of another constituent—such as zinc in brass or tin in bronze—increases. The tendency of silver to raise the annealing temperature of alloys seems to be rather general.

*Resistance to corrosion.* As may well be expected, alloys containing a substantial proportion of silver acquire some of the nobility and corrosion-resistance of silver. It is less obvious, however, that a small proportion of silver may be surprisingly effective in increasing the resistance of a base-metal alloy to corrosion. For example, one per cent of silver, or less, converts lead into an insoluble anode suitable for the electrolysis of acid zinc sulfate solutions, inhibits pitting attack of lead-antimony alloys in sulfuric acid, reduces pitting corrosion of stainless steel and dezincification of brass.

*Hardness and strength.* The effect of silver on the hardness of alloys must be considered from two angles. In one case, silver moderately increases the hardness of soft metals such as tin, lead, zinc, aluminum, magnesium, and copper by an additive effect or a solid solution hardening effect. In the other case, the precipitation of a silver-rich phase, or a silver compound, from solid solution by suitable heat-treatment produces a much higher order of hardness (it is also possible that the presence of silver in solution in the alloy affects the solubility of a precipitable element present in the alloy, and thus, indirectly affects the hardenability). Examples of the second class have been discussed under the copper-silver, copper-tin, copper-zinc, copper-silicon-manganese, copper-beryllium, copper-nickel, aluminum-silver, magnesium-silver, and copper-aluminum alloys. If the base metal is of low solution potential, as is the case for lead, tin, and copper, the presence of silver or a silver-rich phase does not necessarily cause appreciable loss in resistance to corrosion, and hardening is accomplished without sacrifice of corrosion resistance. For alloys whose primary constituent is of high solution potential, as is the case for aluminum- and magnesium-rich alloys, the hardening produced by silver may be associated with a loss in corrosion resistance produced by local couples existing in the alloy. However, the picture is not always so simple, for, as has been mentioned, a little manganese greatly improves the corrosion resistance of magnesium-rich alloys containing silver; also, in those cases where the entire amount of silver is retained in solid solution in the alpha phase, there is no increase, and may even be a decrease in corrodibility of a phase of high solution potential.

Generally, too, when the hardness is increased, the strength is also increased, but the relationship depends on the constitution of the alloy. If the silver is in solid solution, it hardens and toughens the alloy, but the increase in hardness and strength is of a low order compared to the

increase that may be produced by precipitation-hardening. In the Project investigations it was noted that the alloys which became precipitation-hardenable by virtue of their silver content had their yield strength very substantially increased. The tensile strength and hardness increased moderately, while there was a small loss in ductility and electrical conductivity.

*Grain size.* In a number of instances, where the data were available, silver was found to exert a grain-refining effect. This was the case for magnesium-rich alloys, copper-silver alloys, alpha-brasses, the tin bronzes, and the aluminum bronzes. Usually grain refinement is associated with the presence of a finely divided phase insoluble at least in the solid state.

*Grain growth.* It may be expected that when silver produces grain refinement it also tends to restrict grain growth. This was demonstrated for wrought-tin bronzes (Table 22).

*Machinability.* Solid solution alloys of homogeneous structure, and pure metals, are machined with considerable difficulty because the machine turnings do not break off freely and tend to clog the cutting tool. The presence of a finely divided phase, such as lead in brass or sulfides in steel, contributes to improved machinability. Somewhat the same effect is observed in stainless steel and those alloys containing an excess of silver beyond the limit of solid solubility.

*Bonding quality.* By bonding quality is meant the intangible factors involved in brazing and soldering associated with fluidity, capillary flow, and alloying characteristics. Silver added to lead imparts good soldering characteristics, and silver in brass makes a superior brazing alloy. A welding rod of copper containing 1 per cent of silver has superior welding characteristics also.

### 3. Effect of Small Additions to Silver

The effect of adding small proportions of other elements to silver depends to a great extent on the constitution of the resulting alloy. For example, insoluble elements have little influence, other than a possible grain-refining effect (nickel) or improvement in machinability. Elements that enter into solid solution tend to increase moderately the hardness and strength and to toughen the alloy. Elements that form compounds with silver usually increase the hardness substantially, but at the expense of ductility. Elements that enter into solution and also form compounds may make precipitation-hardenable alloys. Elements such as barium, calcium, phosphorus, and sodium may be useful in small percentages as deoxidizers.

The constitutional diagrams given in Chapter 3 are illuminating. Elements that form solid solutions with silver include: aluminum, antimony, arsenic, beryllium, cadmium, copper, germanium, gold, indium, magnesium, manganese, mercury, palladium, platinum, thallium, tin, silicon, and zinc. Elements that form compounds include: aluminum,

antimony, lanthanum, lithium, magnesium, platinum, selenium, strontium, tellurium, tin, and zinc. Relatively insoluble elements include: nickel, chromium, molybdenum, tantalum, and tungsten.

Any of the solid solution alloys, containing no excess of the soluble elements, might be considered for corrosion-resistant applications where better physical properties than are obtainable with pure silver are desired. For example, the resistance of silver to corrosion can be greatly improved by alloying it with soluble noble metals, such as gold, palladium, and platinum, though this is a costly procedure. It is also known that antimony, cadmium, tin, and zinc increase the resistance of silver to tarnish. In general, the chemical nature of both the alloying elements and the corroding environment must always be considered.

The selection of alloying elements to be added to silver for a given application is by no means a simple matter, but in the foregoing discussion, and in the data presented in Chapters 3 and 4, information has been presented which should be helpful.

In conclusion, one point which should not be overlooked is the influence which a lower price for silver would have on its application in the alloy field. Alloys not commercial when silver is selling for five dollars a pound may be economically justifiable at a lower price. In addition, at the lower price, a larger proportion of silver in the alloy can be considered, and thought should then be given to the effect of more than 5 per cent of silver in engineering alloys.



# Chapter 5

## Technology of Silver

A. J. DORNBLATT

### 1. General

This chapter is devoted to a discussion of the mechanical properties of silver and matters pertinent to its commercial production in usable form. No attempt is made to detail procedures to be followed in adapting silver to use, but attention is directed to references in Section C of the bibliography for useful information regarding the technology of silver.

Leach<sup>1</sup> has presented a concise review of the occurrence, economic history, important properties and applications of silver. The manufacture of commercial forms of silver has been depicted in a series of interesting photographs by Christie and Graf.<sup>2</sup> The Handy Book for Manufacturers<sup>3</sup> is a useful reference pamphlet, containing convenient tables of data on the dimension and weight relationships of silver and its industrial alloys, as well as information regarding stamping laws and quality standards for gold and silver. Other general references dealing with the technology of silver include the books by Hoke,<sup>4</sup> Smith,<sup>5</sup> Klein,<sup>6</sup> Percy,<sup>7</sup> and Gee.<sup>8</sup>

Sections 2 and 4 of this chapter include material originally appearing in Circular C 412 of the National Bureau of Standards relating to the mechanical properties and annealing of silver.

### 2. Mechanical Properties

(a) **Elastic Properties.** (1) *Young's Modulus.*—The published values for Young's modulus show considerable variation. Tomlinson,<sup>1</sup> on measuring both annealed and hard-drawn silver, obtained  $7.28 \times 10^{11}$  dynes/cm<sup>2</sup> (converted from Tomlinson's value,  $g$  assumed=980) for the first and for the latter  $7.49 \times 10^{11}$  dynes/cm<sup>2</sup> (calculated from Grüneisen's value,<sup>2</sup>  $g$  assumed=980), but nothing was reported as to heat treatment of the pieces tested. Young's modulus for silver in English units is approximately 10.3 million pounds per square inch.

As shown by Andrews,<sup>3</sup> the value of Young's modulus decreases with increase of temperature of the specimen. The change in modulus is shown in Table 1, reproduced from data presented by Andrews.

(2) *Modulus of Rigidity (Torsion).*—Measurements by Tomlinson<sup>1</sup> of the modulus of rigidity by the torsion pendulum method, yielded  $2.66 \times 10^{11}$  dynes/cm<sup>2</sup> for annealed silver and  $2.69 \times 10^{11}$  for hard-drawn material.



Table 1.—Change of Young's Modulus with Temperature.<sup>1</sup>

Temperature (°C)	Modulus (Dynes/cm <sup>2</sup> ) × 10 <sup>11</sup>	Remarks	Temperature (°C)	Modulus (Dynes/cm <sup>2</sup> ) × 10 <sup>11</sup>	Remarks
30	7.28		448	5.56	
127	7.03		500	5.22	
195	6.95		560	4.22	Slight viscous flow
260	6.52		619	3.40	
324	6.39		680	2.81	Considerable flow.
388	6.21				

As would be expected, this modulus also decreases with rise in temperature. An extended investigation of the variation in torsion properties with temperature was carried out by Kikuta,<sup>4</sup> Table 2.

Table 2.—Change in Torsion Properties of Silver Wire with Temperature.\*

(Length 20.4 cm, diameter 0.503 mm)					
Temperature (°C)	Modulus of rigidity (Dynes/cm <sup>2</sup> ) × 10 <sup>10</sup>	Logarithmic decrement	Temperature (°C)	Modulus of rigidity (Dynes/cm <sup>2</sup> ) × 10 <sup>10</sup>	Logarithmic decrement
27	2.68	0.0041	457	1.93	0.0823
130	2.60	.0175	526	1.80	.1028
189	2.48	.0285	590	1.56	.1278
255	2.40	.0323	655	1.42	.1513
283	2.31	.0324	705	1.26	.1803
327	2.25	.0358	755	1.11	.2071
399	2.14	.0557	811	1.04	.2290

Kikuta's data for hard-drawn wire, 0.465 mm diameter, differ considerably from the values given in Table 2 for annealed metal in that many of the values for the modulus are higher than the corresponding values for annealed metal and the values for logarithmic decrement are quite uniformly much lower.

(3) *Bulk Modulus*.—Both Tomlinson<sup>1</sup> and Grüneisen<sup>2</sup> calculated the bulk modulus  $\kappa$  from the formula  $\kappa = \frac{1}{3}E/1-2\sigma$ , where  $E$  is Young's modulus and  $\sigma$  represents Poisson's ratio. Bridgman<sup>5</sup> measured the linear compressibility of annealed silver directly and found that up to pressures of  $p = 12,000$  kg/cm<sup>2</sup>, the data could be expressed by the formula below:

$$\text{At } 30^\circ\text{C}, \frac{\Delta V}{V} = -10^{-7} (9.87 - 4.4 \times 10^{-5}p) p.$$

$$\text{At } 70^\circ\text{C}, \frac{\Delta V}{V} = -10^{-7} (10.04 - 4.5 \times 10^{-5}p) p.$$

From the formula, the initial compressibility at 30 °C is  $9.87 \times 10^{-7}$  cm<sup>3</sup>kg<sup>-1</sup>. The values for cubic compressibility given in "International Critical Tables" (volume 3, page 46) are, for 30 °C,  $10.20 \times 10^{-7}$  for  $p=0$  and  $9.11 \times 10^{-7}$  for  $p=11,600$  atmospheres. For higher pressures, the compressibility decreases. The reciprocal of the initial compressibility at 30 °C gives a value for bulk modulus of  $9.93 \times 10^{11}$  dynes/cm<sup>2</sup>. This result lies between those of Tomlinson and of Grüneisen.

(4) *Stress-Strain Characteristics*.—Figure 1 shows typical stress-strain curves for silver, obtained by McKeown and Hudson.<sup>6</sup>

(b) *Tensile Properties*.—Data on the tensile properties of silver show marked lack of agreement. One of the most careful determinations of the ultimate tensile strength of annealed silver has been carried out by

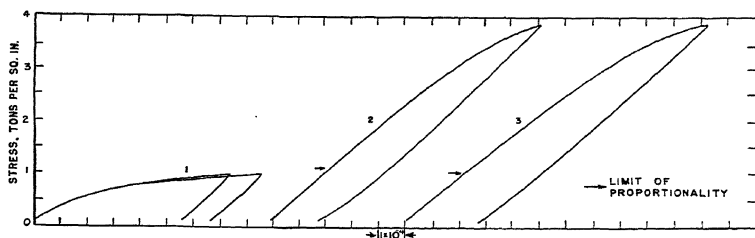


FIGURE 1. Typical stress-strain curves for silver.<sup>6</sup>

Curve 1. Specimen annealed 10 minutes at 500 °C. Curves for 0.1 and 0.01 ton in<sup>2</sup> minute rates of stressing.

Curve 2. Specimen annealed and overstrained 5 per cent in tension.

Curve 3. Specimen annealed, overstrained 5 per cent in tension, and heated one-half hour at 350 °C.

Saefel and Sachs,<sup>7</sup> who reported, for the mean of six determinations, 18,200 lb/in<sup>2</sup>, obtained with samples 5 mm in diameter and 20 mm long, which had been annealed *in vacuo* at 600 °C. Price<sup>8</sup> reported a value a little larger than this. Glocker, Kaupp, and Widmann<sup>9</sup> found about the same strength for 99.7-per cent silver annealed in air at 900 °C, but other values, some of which are several thousand pounds per square inch higher, have been published for supposedly fully annealed material. Values representative of ordinary commercial treatments, as furnished by Handy and Harman, are presented in Table 3 from an article by Rogers.<sup>10</sup> This material probably contained about 99.9 per cent of silver.

A rough approximation to the yield strength was obtained by taking it as equal to the tensile stress at which dividers set for 2 inches pulled out of the punch marks. These values are also given in Table 3.

Table 3.—Effect of Annealing on the Properties of Fine Silver Sheet, 0.032-inch Gauge, Reduced 50 per cent in Thickness after Previous Annealing.<sup>10</sup>

	—Temperature, in degrees Fahrenheit, of 30-minute anneal—							
	As rolled	200	400	600	800	1,000	1,200	1,400
Scleroscope reading	27	27	11			7	6	6
Rockwell no. 1/16-inch ball, 60-kg load	91.0	91.0	49.0	39.0	33.0	30.0	11.5	9.8
Cupping depth (inches)		0.140	0.301	0.328	0.332	0.330	0.331	0.327
Test load (pounds)		750	1,000	1,000	1,000	950	1,000	1,000
Yield strength (lb/in <sup>2</sup> )	44,300		16,000	13,200	11,500	10,600	7,900	7,800
Ultimate tensile strength (lb/in <sup>2</sup> )	54,300		26,500	25,000	25,000	24,100	22,900	22,500
Elongation (% in 2 in.)	2.4		43.7	51.6	51.5	50.8	53.9	48.4

Shoji's <sup>11</sup> measurements on the rate of elongation of a wire of 0.71 mm diameter and 15.7 cm length which had been annealed in hydrogen at 800 °C are summarized in Figure 2. The rate of elongation immediately following the application of the load is plotted against the applied stress. It is evident from the stress at which plastic flow starts that the yield strength of annealed silver is very low. Shoji quotes Tammann's figure of 1,220 lb/in<sup>2</sup> (86 kg/cm<sup>2</sup>) for this property, but apparently made no determination himself.

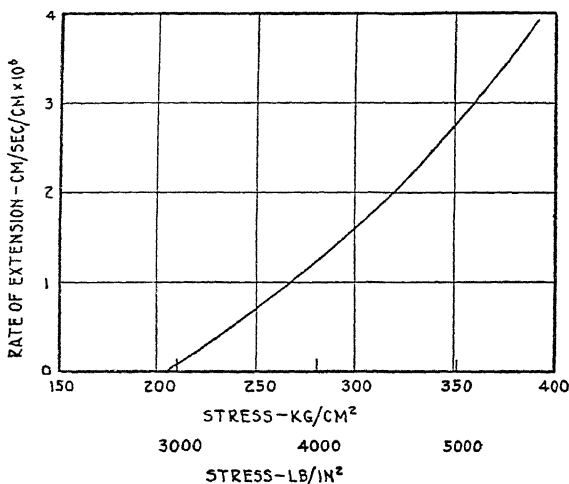


FIGURE 2. Rate of initial elongation of annealed silver wire under tensile stress.<sup>12</sup>

Using samples of silver wire annealed *in vacuo* at 600 °C, Saeftel and Sachs <sup>7</sup> obtained values for elongation, 20-mm gauge length ( $12.5 \times \sqrt{\text{cross-sectional area}}$ ) and reduction of area as follows:

Total elongation	48%
Elongation previous to constriction	42%
Uniform (general) reduction of area (before constriction)	29%
Total reduction of area (including constriction)	91%

Elongation values for commercial material annealed for 30-minute periods are shown in Table 3.

Data on the tensile properties of silver at elevated temperature are given in Table 4, based on information contributed by Handy & Harman.<sup>12</sup> Ingall <sup>13</sup> found that the tensile strength of silver dropped linearly with increasing temperature up to about 160 °C, and at higher temperatures the relationship followed a curved line, the strength decreasing at a faster rate than the temperature increased. Austin and Gier <sup>14</sup> con-

Table 4.—Properties of Pure Silver at Elevated Temperatures.<sup>12</sup>

Temperature (°F)	Tensile Strength (lb/in <sup>2</sup> )	Elongation (% in 2")
Room	47,350	7.0
200	42,050	8.5
400	32,900	11.7
500	15,600	42.2
600	15,300	41.4
800	12,000	37.5
1000	8,200	39.0
1200	3,500	28.9

Specimens were of 99.95% silver, 14-gauge sheet, hard-rolled, and were tested while at the indicated temperature.

ducted creep tests on fine silver (99.9 per cent). These authors presented data illustrating how the temperature-time curves, obtained by means of a modified form of the Rohn test and resulting from plastic deformation, serve as a ready means of making comparisons of the creep characteristics of metals at elevated temperatures. The creep characteristics of single crystals of silver have been investigated at the National Bureau of Standards.<sup>15</sup> The rate of creep, at 400 °C, was found to be influenced by the direction of the stress in the crystal relative to the crystal axes.

(c) **Poisson's Ratio.**—Tomlinson<sup>1</sup> observed the ratio of the lateral contraction to the longitudinal extension in tension for specimens of silver and obtained, for annealed material, a value of 0.369 and, for the hard-drawn, 0.392. Grüneisen's<sup>2</sup> determination by the static method led to a value of 0.379, and by calculations based on dynamically measured quantities he obtained a value of 0.369.

(d) **Compression Properties.**—Coe<sup>16</sup> determined the changes occurring during compression for hard-drawn silver and also for silver which had been annealed for 30 minutes at 800 °C. He plotted load on the compression specimens against the corresponding decrease in length of the specimen and found that the resulting curves showed a peak, representing the maximum rate of flow. The stress immediately preceding this maximum rate has been designated by Coe as the "stress giving critical plasticity." His data, on samples 1 inch long by  $\frac{1}{2}$  inch diameter, are summarized in Table 5.

Table 5.—Properties of Silver When Compressed.<sup>16</sup>

Condition	Elastic Limit (lb/in <sup>2</sup> )	Stress Giving <sup>1</sup> Critical Plasticity (lb/in <sup>2</sup> )	Reduction in Length at Stress Giving Critical Plasticity (%)	Density (g/cm <sup>3</sup> )	Brinell Number (10-mm, 1,000-kg, 60-sec)
Drawn	15,700	40,300	21.6	10.510	72.5
Annealed	600	42,500	31.1	10.506	29.0

<sup>1</sup> Stress for maximum decrease in length for a unit increment of load.

(e) **Hardness.**—The resistance of silver to indentation has been determined by a number of observers. Kurnakow and Achnaserow<sup>17</sup> reported

a Brinell number of 27.0 for slowly cooled, annealed silver and 24.4 for rapidly cooled material. Tammann and Dreyer<sup>18</sup> have given a Brinell number of about 32 for material annealed for a short period at 300 °C. Coe (Table 5) obtained a value of 29 for annealed silver. Other experimenters, for example, Glocker, Kaupp, and Widmann,<sup>9</sup> have reported considerably higher values. Brinell readings on silver in the annealed condition and also after being rolled to various reductions are shown in Figure 3; these are based on data obtained by Holzmann.<sup>19</sup> Holzmann

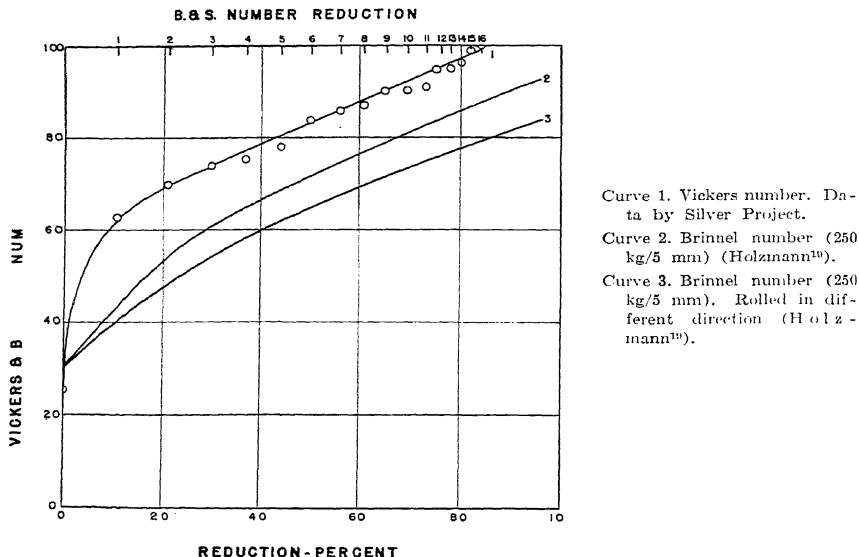


FIGURE 3. Relation between hardness of silver and the degree of reduction.

used a 250-kg load and 5-mm ball, which makes comparison with other data based on the 500-kg load and 10-mm ball inexact. Data obtained by the Project, using the Vickers machine, have also been plotted in Figure 3 for comparison. Data on the scleroscope and Rockwell (60-kg,  $\frac{1}{16}$ -inch ball) readings of silver after various annealing treatments were given in Table 3.

(f) **Miscellaneous Mechanical Properties.**—Data on the depth of impression in cupping tests for material rolled through different reductions are given in Figure 4 from Holzmann.<sup>19</sup> The decrease of depth of impression with reduction in thickness in the early rolling is about as expected. The reason for the minimum which occurs is not clear.

In an investigation of non-abrasive wear, which occurs in polishing metals, Hudson<sup>20</sup> found that silver plating was less resistant than

platings of palladium, platinum, or nickel. Another interesting investigation worthy of mention is that of Lonsdale<sup>21</sup> on the change of dimensions of silver and other wires subjected to torsion.

### 3. Melting, Deoxidation and Casting

Molten silver has the ability to dissolve about twenty times its own volume of oxygen, and, if it has been permitted to become saturated with this gas, it will liberate almost all of it rather suddenly when it reaches its freezing point and begins to solidify. This sudden liberation of large quantities of dissolved oxygen produces the phenomenon described as "spitting" or "spurting." Naturally, an ingot cast under such conditions would be quite porous and useless. To avoid porosity in silver castings it is necessary that precautions be taken to minimize contact between

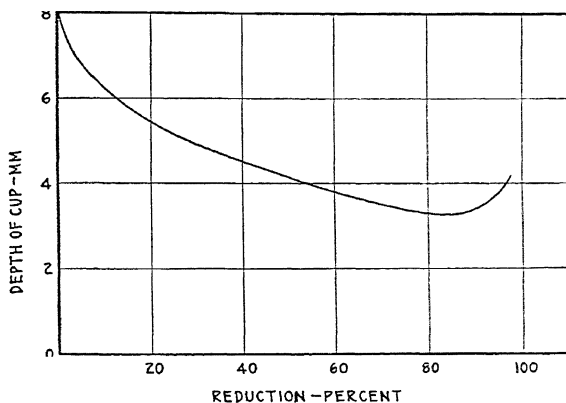


FIGURE 4. The cold-deformability of silver by cupping test as a function of the degree of reduction by rolling in one direction (Holzmann<sup>19</sup>).

silver and oxygen; and, where complete absence of oxygen cannot be assured, the molten metal must be deoxidized before attempting to cast it into a mold. The deoxidation of silver and its technical alloys has been studied and discussed by Raub, Klaiber and Roters,<sup>1</sup> Roters,<sup>2</sup> Long,<sup>3</sup> Guichard,<sup>4</sup> Leach and Chatfield,<sup>5</sup> Smith and Turner,<sup>6</sup> and others.

Further references to the influence of gases on silver is made in section 5 of this chapter.

Certain types of defects found in silver or silver alloy sheet can occasionally be traced to faulty melting, deoxidation, or casting practice. Such defects in silver alloys have been discussed by Raub,<sup>7</sup> Moser, Raub, and Frohlich,<sup>8</sup> Streicher,<sup>9</sup> and others.

Since the greater part of all silver handled in technical practice is in the form of sterling and coin silver containing respectively 7.5 and 10 per

cent of copper, much has been published relating to melting practice to be used in handling copper-silver alloys. In addition to the references given in section C. 3 of the bibliography, attention is also called to references appearing in section B. 13.

#### 4. Mechanical and Thermal Processing

(a) **Temperature of Annealing.**—The temperature at which the properties of cold-worked silver begin to change to those of the annealed metal has formed the basis of a number of investigations. Although the temperature of this change depends, in large measure, on the chemical purity and degree of cold-working of the metal, it has been found to vary considerably according to the property selected as the criterion.

Measurement of one or more of the mechanical properties is the common method for detecting the onset of changes brought about by heating. For example, the hardness of cold-worked silver diminishes when the silver is heated at a particular temperature, which depends, in part, upon the duration of heating at this temperature. Tammann and Dreyer<sup>1</sup> found that softening could be detected after 1-hour periods at the temperatures indicated in Table 6.

Table 6.—Effect of Prior Cold Work on Annealing Temperature.<sup>1</sup>

Reduction by Rolling at 20 °C (%)	Temperature at which softening begins (°C)
90	65
50	100
10	250

Extremely long periods at these temperatures are required to produce a marked decrease in hardness. From facts to be brought out shortly, it appears doubtful whether complete annealing could ever be effected at the temperature at which initial effects are observed.

The effect of temperature on cold-worked silver containing 0.2 per cent of copper and some iron was studied by Glocker, Kaupp, and Widmann,<sup>2</sup> whose curves showing the changes in ultimate tensile strength, per cent of elongation, and grain size, as replotted by Clark<sup>3</sup> are shown in Figure 5. It will be noted that marked changes in the mechanical properties resulted on annealing at approximately 200 °C. That this temperature is by no means as definite as might be supposed is evident from the authors' statement that in a previous experiment annealing was observed at 150 °C on the same material which had been reduced 97 per cent in thickness instead of 99 per cent as in the present case.

The effect on commercial silver (99.9 per cent of silver) of annealing for half-hour periods has been given in Table 3. The decrease in hardness and strength, and corresponding changes in other properties, continue to comparatively high temperatures.

Data obtained by the Project on the annealing characteristics of silver of at least 99.995 per cent purity are shown in Figure 6. The annealing temperature is lowered by increasing amounts of cold reduction, but the final hardness is higher in the annealed material which had been most severely worked.

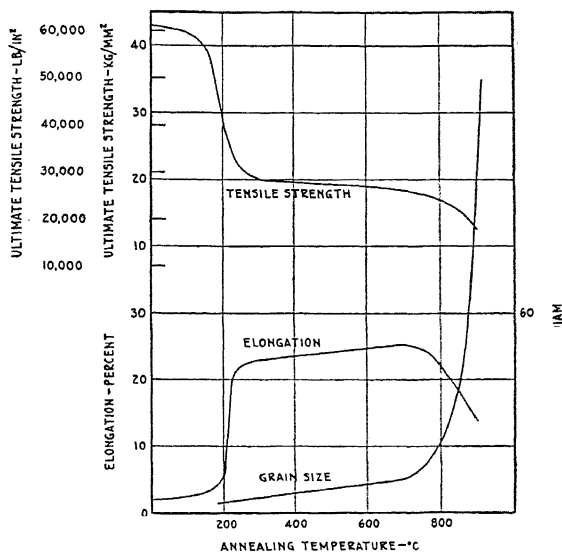


FIGURE 5. Tensile strength, elongation and grain size of rolled silver sheet as functions of annealing temperature. Clark,<sup>2</sup> from Glocker, Kaupp, and Widmann.<sup>3</sup>

Annealing affects different properties at different rates. Thus, Tamman and Dreyer,<sup>1</sup> who observed a change in the electrical resistance of cold-worked silver after 5 minutes at 60 °C and a marked decrease after short periods at 100 °C, state that the electrical resistance reaches the value of the annealed state and the hardness decreases half-way to its value for the annealed condition before any change in the microstructure can be observed.

Other properties change when cold-worked metal is annealed. For example, Tamman and Bandel<sup>4</sup> made thermocouples composed of annealed silver against cold-worked silver. With wire that had been reduced 90 per cent by drawing they found that annealing effects appeared at 100 °C when the rate of heating was 2.5° per minute. Margenau<sup>5</sup> studied the effect of plastic deformation on the wave length at which the minimum reflecting power of silver occurred and found that the minimum for the deformed material occurred with a wave length 20 Å smaller



than for annealed metal. Magnetic susceptibility, temperature coefficient of resistance, and other properties are also functions of the degree of annealing and have been discussed in connection with the information on these various properties.

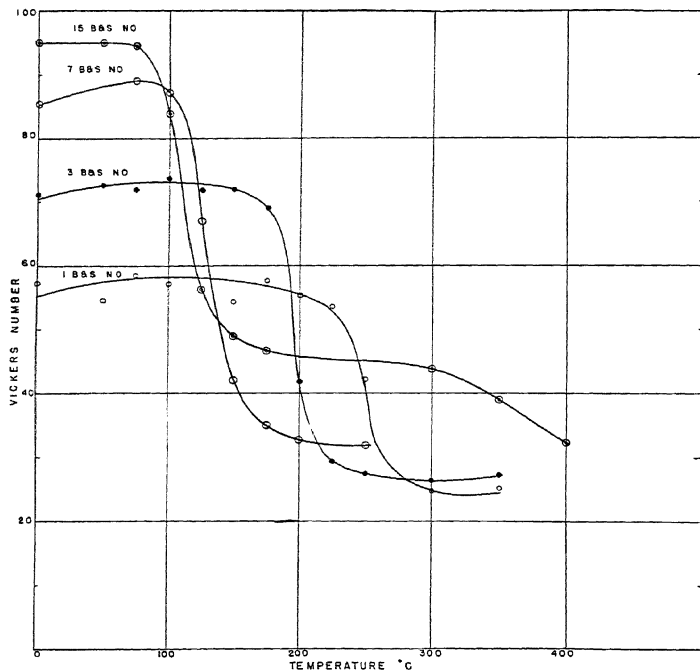


FIGURE 6. Influence of prior cold deformation on annealing of silver.

Curves for 1, 3, and 7 B. & S. numbers reduction based on data obtained on annealed sheet, initially number 15 B. & S. gauge.

Curve for 15 B. & S. numbers reduction based on data obtained by cold-rolling annealed silver, initially number 00 B. & S. gauge.

(b) **Recrystallization and Structural Changes.**—Changes in the crystalline state of silver may be studied either by x-ray or microscopic methods. Nishikawa and Asahara<sup>6</sup> examined thin sheets of silver by passing a beam of x-rays perpendicularly through the sheet and found a preferred orientation in the space lattices of the existing crystal grains. They also discovered that the pattern obtained after the sheets had aged for 3 weeks at room temperature was distinctly different from that of freshly rolled sheets.

Experiments of Glocker and Kaupp<sup>7</sup> on sheets which had been

reduced 97 per cent indicated an initial change after 10 minutes at 140 °C. The maximum intensity of the spots constituting the x-ray diffraction pattern of the rolled silver began to diminish after 10 minutes' heating at 170 °C. However, complete removal of the rolled structure could not be accomplished by very long annealing periods at approximately 300 °C and persisted up to 700 °C, according to these authors. No trace of the rolled structure was observed after 10 minutes at 830 °C, but Holla-baugh<sup>8</sup> considers this temperature to be insufficient to produce a completely random distribution. According to him, a temperature of 900 °C is necessary if the period of annealing is not to exceed one-half hour.

Glocker, Kaupp, and Widmann<sup>2</sup> used both x-ray and microscopic methods. On the basis of the x-ray results, on silver of about 99.7-per cent purity, with 10-minute annealing periods, they recognized three stages in the annealing of rolled sheet silver:

1. The cold-rolled condition for which the pattern of the as-rolled material persists up to about 200 °C.

2. The partly annealed state, from 200 to about 800 °C, in which a definite orientation somewhat different from that of the cold-rolled material persists.

3. The condition of random distribution of the space lattice of the grains. The lower temperature limit cannot be stated with certainty, since the change from the x-ray pattern of the partly annealed state to that of a random distribution is very gradual.

No change in the visible microstructure could be detected until an annealing temperature of 212 °C had been reached. At this point, some indication of new crystals was observed at a magnification of 1500 diameters. With increase in the annealing temperature, recrystallization proceeded, but with no marked grain growth until, at about 800 °C, marked grain growth set in. This tendency became pronounced with very high annealing temperatures, Figure 5.

Table 7.—Annealing Temperature of Silver Containing Various Impurities

Element added	Amount (%)	Recrystallization temperature (°C)	Element added	Amount (%)	Recrystallization temperature (°C)
None	...	150	Nickel	0.1	137
Copper	0.303	230	Gold	.1	112
Copper	.012	200	Gold	.2	110
Copper	.073	175	Palladium	.1	112
Aluminum	.20	190	Iron	.035	110
Zinc	.119	145	Iron	.055	20
Lead	.059	145	Iron	.065	20

(c) **Composition vs. Annealing Temperature.**—The presence of small percentages of other elements appears to alter the temperature at which annealing effects set in as determined by the x-ray method, as shown by the data in Table 7 from Widmann,<sup>9</sup> which have been confirmed by Clark.<sup>3</sup>

The temperatures given refer to severely cold-worked material. One statement of Clark's is noteworthy, which is to the effect that silver containing less than 0.0005 per cent of iron and 0.00002 per cent of lead recrystallizes at room temperature.

The effect of larger percentages of some elements on the annealing temperature of silver was shown in Figure 5 of Chapter 3.

(d) **Orientation of Crystals in Cold-worked Silver.**—The tendency of the crystal structure of cold-drawn silver wire to be definitely related to the direction of drawing, that is, to exhibit "preferred orientation," was observed by Ettisch, Polanyi, and Weissenberg.<sup>10</sup> A more detailed study

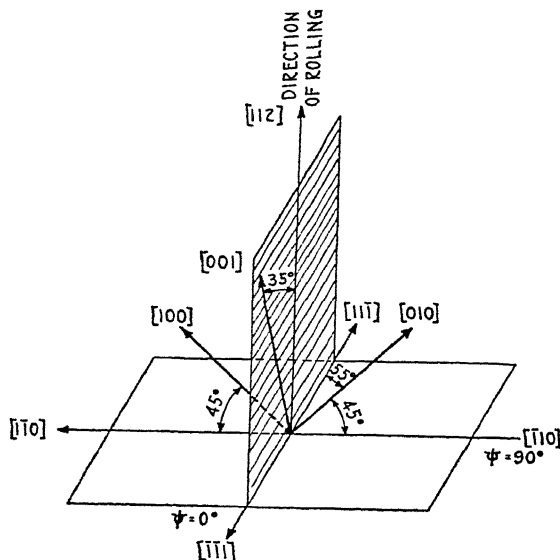


FIGURE 7. Preferred orientation in the grain structure of rolled silver sheet with respect to lattice directions. (Glocker.<sup>12</sup>)

was made by Schmid and Wasserman,<sup>11</sup> who stated that the crystals tend to arrange themselves in such a way that either the (100) or (111) planes are approximately parallel to the axis of the wire. These authors also concluded that about 75 per cent of the crystals were grouped according to the former arrangement and about 25 per cent in the latter.

Studies of the preferred orientation of the crystals in cold-rolled silver sheet by Mark and Weissenberg,<sup>12</sup> by Glocker,<sup>13</sup> and by Glocker, Kaupp, and Widmann<sup>2</sup> have given results in good agreement with one another. Figure 7 from Glocker's data is representative. The shaded area repre-

sents the rolled sheet or foil, the direction of rolling being indicated by the vertical arrow. The preferred orientation of the face-centered cubic crystals is such that the arrow representing the direction of rolling also indicates the (112) direction of the lattice. It will be noted that the (111) direction lies in the plane of the foil and is transverse to the direction of rolling and that the (110) direction is perpendicular to the plane of the sheet. The heavy arrows represent the axes with respect to which the other directions are defined.

Actually, there are two preferred orientations of which Figure 7 may be considered to be the first. The second is described by a figure which is the mirror image of Figure 7 with the reflection taking place across the plane which contains the direction of rolling and the perpendicular to the sheet.

When sheet silver is annealed at a low temperature, the relations described above are replaced by four preferred orientations. In the new orientations, the (112) planes are still approximately in the direction of rolling, but the (311) family of planes has moved into practical coincidence with the normal to the foil. Annealing at a sufficiently high temperature will, of course, produce a completely random distribution of crystal lattices.

## 5. Effect of Gases

Smithells<sup>1</sup> has summarized and discussed the data in the literature on gases and metals, and his book is recommended as a source of information dealing with the effect of gases, such as hydrogen and oxygen, on silver. Section C. 5 of the bibliography should be consulted for references to the original investigations.

Molten silver at the melting point absorbs about 20 times its own volume of oxygen, according to Sieverts and Hagenacker,<sup>2</sup> that is, about 200 cc per 100 grams of silver. Steacie and Johnson,<sup>3</sup> who measured the solubility in solid silver, concluded that there was no abrupt change in solubility at the melting point, but merely that the solubility curve was very steep in this region. The solubility 50 °C below the melting point is only about 10 cc per 100 grams, and there is, therefore, a very large evolution of gas when the metal is solidifying. The pressure of oxygen liberated in the interior of a solidifying ingot is sufficient to eject globules of the still molten metal through the solid crust. A minimum in the solubility curve occurs at 400 °C, below which temperature a stable oxide, Ag<sub>2</sub>O, probably exists. Steacie and Johnson found that the solubility was proportional to the square root of the pressure at pressures above 10 mm. Johnson and Larose<sup>4</sup> measured the rate of diffusion of oxygen through solid silver plates and found a square root relation between the rate of diffusion and the pressure. It was shown that their data on the diffusion of the gas through the metal was in accord with Richardson's equation. Neither nitrogen nor hydrogen appear to be adsorbed on silver, but Benton and Drake<sup>5</sup> found a significant adsorp-

tion of oxygen on silver, accompanied by a heat of adsorption of 2000 to 3000 calories per gram molecule. The adsorption of oxygen on silver is of importance in relation to the catalytic activity of silver, and also to the oligodynamic activity. This latter point is discussed in Chapter 16.

As silver has a very high solubility for oxygen, consideration must be given to this fact in processing silver and its alloys. Silver alloys are less troublesome than pure silver as regards spitting or porosity due to oxygen, because of the effect the added elements have on the solubility of oxygen in the molten metal. As the elements, such as copper, normally present in the alloys are more reactive than silver, they tend to act as deoxidizers. Even 0.1 per cent of copper in fine silver is found to be beneficial in melting and casting practice. Copper is not an adequate deoxidizer; hence the silver-copper alloys must be properly deoxidized if they are to possess good ductility and surface finish, and be free from objectionable features found in insufficiently deoxidized metal.

Aside from promoting porosity in the ingot, oxygen is also objectionable because it will combine with any hydrogen that may be present in the gases to which the metal is exposed in annealing (moisture in the air must also be considered as a possible source of hydrogen), and the formation of water vapor by interaction of the hydrogen and oxygen produces blisters. If the silver is alloyed with copper, for example, then some oxygen may be present as cuprous oxide, and a similar reaction occurs, liberating water vapor and producing defective material. In welding fine silver, it is important that the atmosphere in the immediate vicinity of the fused metal be non-oxidizing, as an oxidizing atmosphere will result in a porous weld.

Since oxygen not only dissolves in molten silver, but also has the property of diffusing through solid silver, the penetration of silver coatings by oxygen at elevated temperature may require special consideration. This matter is discussed at more length in Chapter 10.

Hydrogen, which is readily absorbed by iron, nickel, cobalt, and copper in the solid state, is absorbed to a less extent by silver. There is a large increase in solubility when the metal melts. In these metals solution is a completely reversible process; the solubility is proportional to the square root of the gas pressure, and follows an exponential law. Steacie and Johnson<sup>6</sup> determined the solubility of hydrogen in silver at temperatures between 200 and 900 °C, and at pressures between 5 and 80 cm of mercury. At a temperature of 750 °C and a hydrogen pressure of 80 cm of mercury, the solubility was  $\frac{1}{4}$  volume of hydrogen.

Although the solubility of hydrogen in silver is relatively small, it may be of some consequence in special instances, such as in the manufacture of products from metal powders, where a hydrogen atmosphere is frequently used.

Nitrogen is insoluble in silver<sup>3</sup> and would make a suitable inert atmosphere where no contamination by dissolved gases is permissible.

## 6. Metallography

Information concerning the laboratory technique for metallographic examination of silver and its alloys is, unfortunately, lacking in convenient form. For the most part, observations in the literature relating to polishing and etching procedures used are widely scattered. However, it is quite likely that a technique which is satisfactory for polishing soft metals like lead and magnesium would work well with silver. Ellinger and Acken<sup>1</sup> have described a method for preparing metallographic specimens that is particularly adapted to soft metals. The etching of silver requires that an agent be selected which will attack the metal, and yet not cause pitting. An electrolytic etch, using a 5-per cent KCN solution is generally satisfactory. The structure of silver coatings on steel can be examined by etching the section first with a solution of 5-per cent nitric acid in alcohol, and then using the electrolytic etch with the specimen in contact with a platinum wire anode while immersed in aqueous 5-per cent KCN solution. Because of the softness of silver, the effect of the polishing distortion will persist to some depth below the surface, and the flow of metal in polishing should be kept to a minimum to avoid the necessity of many repeated polishing and etching operations.

Patchin<sup>2</sup> has pointed out the utility of metallographic examination, particularly with reference to silver and other noble metals and their alloys.

## 7. Fabrication of Silver Equipment

Silver is commercially available in sheet, plate, rod, and tubing of adequate size for chemical plant fabrication. It has also recently become commercially available in a range of sizes of plate composed of a cladding of silver on a base metal such as copper, nickel, or steel. Because of the necessity for protection against contamination by base metals, silver equipment is fabricated by fusion welding, using fine silver filler-rods or, where the environment permits, by corrosion-resistant silver brazing alloys. This subject is discussed at more length in Chapter 7. The manufacture of clad steel sheets has been discussed by Schone and Radeker,<sup>1</sup> and Leach<sup>2</sup> has discussed applications of silver in chemical plants, and the manufacture of clad metals. Forstner<sup>3</sup> has reviewed the subject of silver coatings, and has discussed the fabrication of silver equipment.

The fabrication of silver equipment is usually undertaken by skilled coppersmiths or, in some of the plants using large amounts of silver equipment, by a specially trained crew. Those experienced in fabricating equipment of solid silver liken the welding of the silver to lead-burning, and consider it no more difficult.

## 8. Surface Tension and Viscosity

Section C. 8 of the bibliography contains references relating to the surface tension and viscosity of silver and its alloys. These properties

are of particular importance in relation to brazing and sintering phenomena.

## 9. Diffusion

Section C. 9 of the bibliography contains references to studies of diffusion phenomena in silver and related alloys. The response of alloys to heat-treatment, the bonding of dissimilar metals, and migratory changes taking place at an interface involve diffusion processes.

In concluding this chapter, attention is called to the discussion of bonding and brazing in Chapters 6 and 7, and of electroplating in Chapter 10.

## Chapter 6

# Low-Temperature Bonding of Silver

By ALLISON BUTTS \* AND G. R. VAN DUZEE †

One of the valuable qualities of silver which may lead to further applications in industry is the ease with which it may be welded or bonded at only slightly elevated temperatures, or even at room temperature under proper conditions. In some uses of silver this behavior may operate as a disadvantage in causing sticking of silver surfaces in contact. In addition to a discussion of the cold bonding properties, there will be given in this chapter some quantitative data thereon obtained in the metallurgical laboratory at Lehigh University by the writers and by J. M. Thomas.

In considering applications of bonding properties, it is desirable to have an understanding of what constitutes a bond in the joining of two metal surfaces, how the bonding is related to the metallic structure, and what the factors or conditions are which affect it.

All metals in the solid state are crystalline aggregates. The metal atoms are subject to interatomic forces, usually called "atomic bonds," which cause them to assume in the solid state certain positions which constitute a pattern or "space lattice" characteristic of a group to which the metal belongs. In the liquid phase these bonds do not exist and the atoms are free to move almost at random. When the liquid metal solidifies, or when the metal is electrolytically deposited, the atoms are drawn into the lattices and the association of millions of lattices forms a metallic crystal. Ordinarily the crystals interfere with one another in growth so that they do not assume visibly a typical crystalline form, but instead are compacted and often rounded into grains. At the interfaces of the grains and at the external surface of the metal there are incomplete and perhaps distorted lattices whose atomic bonds will exert a cohesive influence on similar lattices of another metal surface if brought sufficiently close, that is, into sufficiently intimate contact.

The joining of two metal surfaces to form a single piece may be brought about (1) by fusion welding, in which the atoms at one surface can mingle freely with those of the other surface and form a continuous crystalline aggregate when the fused metal solidifies; or (2) by soldering or brazing, in which the atoms of the liquid soldering or brazing alloy

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† Instructor in Metallurgy and former Silver Research Fellow, Lehigh University.



may readily join the lattices at the solid metal surfaces; or (3) by pressure welding, in which the surfaces in the solid state are merely brought into sufficiently intimate contact, commonly by the aid of both pressure and heating, to enable a mutual knitting of their lattices. Only the third method is to be discussed in this chapter. In this method the union of the surfaces is partly a result of the atomic bonds or forces exerted and partly a result of diffusion of the atoms of one surface into the lattices of the other. In joining two metals that are physically and chemically alike there may be no diffusion apart from the transfer of atoms brought about by the atomic bonds; in joining unlike surfaces there may be the more pronounced diffusion which seeks to bring about physical and chemical equilibrium.

While intimacy of contact is thus the *sine qua non* of pressure welding, there must be considered also the factors which are known to affect greatly the process of being joined in this way. These are (1) cleanliness or the absence of foreign substance (including gas) between the surfaces; (2) plasticity of the metal; (3) temperature; (4) pressure; (5) time; (6) recrystallization.

### Absence of Foreign Substance

The contact necessary for the union of two surfaces must be contact between metallic crystals or lattices; the presence of any non-metallic substance will obviously prevent this contact. The non-metallic substance may be dirt, grease, or similar foreign matter; or it may be a film (usually oxide) chemically formed on the surface; or it may be gas molecules (usually air or oxygen) adsorbed on the surface. If present only in spots instead of continuously, it may only partially interfere with the bond and weaken it somewhat instead of preventing it entirely. The use of flux to dissolve oxide films and remove dirt is a common and frequently an essential step in the processes of soldering and welding. Careful cleaning of the basis metal for electroplating is known to be essential for uniformity, continuity, and good adherence of the deposit. The effect of gas adsorption on surfaces is less widely known and not so well understood, but nevertheless has been pointed out by several writers. Bancroft<sup>1</sup> has discussed it at some length. Dean<sup>2</sup> states that "if it were not for adsorbed gas, welding could be done at room temperature." In dental practice it is found necessary to heat gold foil to redness (then allowing it to cool) just before consolidating it by pressure in a gold filling.<sup>3</sup> Similar advantage in heating silver to redness before cold welding is shown in the experimental work on silver described on a later page. The effect of heating is to decrease the adherence of adsorbed gas and presumably to expel the gas entirely if carried far enough.

In studying the friction of nickel on nickel in a vacuum, Holm and Kirschstein found that cold-welding of the nickel surfaces occurred readily, so much so as to interfere with an inclination method of studying

frictional adhesion, and they were forced to use a method in which force was applied parallel to the contacting surfaces.<sup>13</sup>

### Plasticity

Capability of plastic flow under applied force is a distinctive property of ductile metals. Plasticity implies easy deformation without rupture and permits intimacy of contact between surfaces pressed together by allowing them to conform in minute detail. Comstock<sup>4</sup> states that plasticity is important in welding not only because it promotes intimate contact but also because the arrangement of atomic forces and the atomic mobility incident to plasticity are favorable for the propagation of atomic bonds between the surfaces.

### Temperature

Since heating (short of fusion) increases plasticity, temperature becomes an important factor in welding in promoting intimacy of contact. It is equally important in other particulars. The effect of heating in displacement of adsorbed gas has been noted above. Rates of diffusion and of crystal growth increase greatly with temperature. Temperature is also a factor in recrystallation, as noted below. It is important to observe that temperature is an indirect factor in all these particulars. Elevated temperature therefore promotes pressure welding, but is not an essential condition.

### Pressure

Application of pressure supplements heating and plasticity in bringing about the required intimacy of contact. Practically, some degree of pressure is necessary. For a given metal the same result in welding may in general be brought about by high pressure at low temperature or by low pressure at high temperature. For different metals, the greater the plasticity at a given temperature the lower the pressure that will be needed.

If the surfaces are ground flat to the degree possible with optical glass, both pressure and heat may disappear as factors. Surfaces of glass, copper, and other substances have been prepared in this manner, and when they are simply brought into firm contact with a like surface, a bond strong enough to support a heavy load has resulted. Spring<sup>5</sup> found that two cylinders of the same metal accurately faced and cleaned would adhere firmly when pressed lightly together at ordinary temperatures and would become firmly united on heating. This union was so strong that separation of the cylinders by force caused a fracture through the metal on one side or the other of the junction.

Pressure is also effective in displacing adsorbed gas from the surfaces. This is shown in the work with silver, wherein it was found that a strong bond was obtained either by using a higher pressure without having removed gas by prior heating or by using a lower pressure after heating.

This effect of pressure, however, will not necessarily hold in all cases; it will doubtless depend on the tenacity with which the gas is held on the surface, which in turn will depend on the metal, the gas, the temperature, and the condition of the surface.

Pressure will also offset the effect of other foreign matter if the latter does not form a continuous coating, and permit bonding in spots where clean metal contact is produced between the coated areas.

### Time

Time is an important factor in producing a strong bond in pressure welding. It is not an essential factor, as instantaneous welds may be produced under favorable conditions. The effect of time appears to depend on its increasing the extent of plastic flow, diffusion, and crystal growth. The last two are relatively slow and their chief result is to strengthen a bond already established to some degree; time and temperature work together in furthering them. Time also is a factor in recrystallization.

### Recrystallization

Under certain conditions the crystals which make up a metal will break down and form new crystals by rearrangement of the atoms into new lattices or by rearrangement of the lattices themselves. New crystals grow from new crystal nuclei. This occurs in allotropic change, and is then accompanied by a liberation or absorption of heat. It is also believed that no allotropic change occurs in silver, though some investigators have reported the detection of one. Recrystallization sometimes occurs when the metallic crystals have been strained and distorted, as by cold work. If the metal is heated, it may occur after very slight strain. Recrystallization after cold work releases internal stress and causes disappearance of the hardness which the cold work produced. The recrystallization temperature varies for different metals from below room temperature to very high temperatures. For any one metal it may be lowered greatly by cold work. For tungsten the *minimum* recrystallization temperature is said to be 1200 °C. For silver only slightly strained it is believed to be about 200 °C; the decrease after cold work may perhaps bring it close to room temperature if carried sufficiently far. Experimental data on the softening temperature of cold-worked silver are given in Chapter 5. It may readily be seen how recrystallization occurring at a bonded junction may increase the strength of the bond by knitting of the crystals across the junction during the readjustment. That this is actually an important factor in producing a strong bond has been shown in the "welding" or consolidating of silver powder through pressure. If the powder is alternately pressed cold and heated, thus causing alternately cold work and recrystallization, the strength of the consolidation is progressively increased.

Grain growth across a bonded junction may have a similar effect.

Recrystallization often results in a finer grain than existed before; grain growth will then ensue if a temperature which permits it is maintained. Grain growth may also occur without recrystallization having preceded it.

### Strength of Bonding

From the foregoing discussion of the nature of bonding, it may be seen that the strength of a bond may vary all the way from a slight adherence or sticking up to the full strength of the body of the metal. There is no fixed point where the joined surfaces may be said to be completely bonded and below which the weld must be called incomplete. Any such designation must be arbitrary and relative, but for practical purposes some arbitrary test of strength may be used to designate or classify the strength of the union. With material of suitable size a tensile test may be used.

### PROPERTIES OF SILVER AS A MATERIAL FOR BONDING

For low-temperature bonding of suitable strength silver is superior to all other metals except gold. The properties which in combination account for its weldability include its chemical nobility, plasticity, and low temperature of recrystallization after work-hardening. Whether there are other contributing factors of importance is not known. Experimental work described on another page has indicated that adsorbed oxygen or air is readily removed from its surface by simple preheating, and there is no danger of forming a hindering oxide film on silver in a heating treatment of this kind. Silver is not attacked by air or even by pure oxygen, either dry or moist, at ordinary temperatures and pressures. A black silver oxide coating may be formed with ozone or by using silver as an anode in electrolysis in sulfuric acid at moderate to high current density; at lower current density silver dissolves without oxidation. Silver is just below mercury in the electropotential series of metals and its potential of 0.80 volt is exceeded in nobility only by those of platinum and gold among the common elements. The heat of formation of silver oxide ( $\text{Ag}_2\text{O}$ ) is only 434 cal. per gram-atom of oxygen, far lower than the comparative figure of 1063 cal. for platinum oxide ( $\text{PtO}$ ), but higher than that of gold oxide ( $\text{Au}_2\text{O}_3$ ), which is the only oxide having a negative heat of formation.

Tronstad and Höverstad<sup>6</sup> examined by optical methods the surfaces of metals slowly heated and found in the case of silver certain changes, which they attributed to oxidation, occurring up to 180 °C, after which the change was reversed, apparently due to decomposition of the oxide. This temperature corresponds to that determined by Keyes and Hara<sup>7</sup> as the temperature of decomposition of silver oxide with a dissociation pressure of 1 atmosphere. This would indicate the possibility of formation of some oxide on the surface of silver when heated for some time

below 180 °C, with the disappearance thereof above that temperature. On the other hand, Dobinski,<sup>8</sup> in a study of the structure of polished metal surfaces, found that exposure of the surfaces of most metals to air either during or after polishing affected the electron diffraction pattern because of oxidation, but that in the cases of both gold and silver there was no such effect.

The combination in silver of plasticity and fairly high tensile strength is notable. Silver is stated to be surpassed only by gold in the related properties of ductility and malleability. The ultimate tensile strength of silver when fully annealed is about 22,500 pounds per square inch, which is close to that of copper and above that of gold. Sufficient cold-rolling will increase this figure to over 54,000 pounds per square inch. Though its tensile strength is thus very satisfactory for ordinary structural uses, it yields more readily than most metals to plastic flow under applied pressure. Though its plasticity of course increases with heat, it retains its strength well at moderately elevated temperature. The strength of silver is an important consideration in the possibility of using silver as a structural part for the purpose of making a surface that may be bonded at low temperature.

The crystal form of silver belongs to the face-centered cubic system. This group includes also the metals gold, copper, nickel, lead, aluminum, cobalt, platinum, palladium, rhodium, calcium, cerium, thorium, and gamma iron.

#### EXPERIMENTAL STUDY OF LOW-TEMPERATURE BONDING OF SILVER

A quantitative study of the time-temperature-pressure relationship in firm bonding of silver was made by the writers as a part of the work sponsored by the Silver Producers' Research Project at Lehigh University. Since previous experimental work had shown the importance of surface condition, some preliminary experiments were carried on to determine the condition most favorable for welding. This was done by rolling two strips of silver in contact while hot. The strips to be welded were heated to the desired temperature in an electric muffle furnace and then passed through the rolls. It was found that strips heated to 400 °C and then rolled, receiving about a fifty per cent reduction in area, formed an adherent bond. With lower preheating temperatures, a satisfactory bond was not obtained by a single roll pass, although a slight sticking of the surfaces was evident. This sticking could then be converted into an adherent bond, without further heating of the strips, by further reduction in the rolls.

#### Effect of Surface Condition

In this method of bonding, the surface condition of the silver did not seem to be of importance, other than that it be reasonably clean and of a smoothness readily obtained by ordinary polishing methods. Strips polished on No. 1 emery paper gave a bond of adherence equal to that

obtained with strips ground on successive grades of emery paper ranging from No. 1 to No. 000. It is probable that the rolling operation caused sufficient "flow" of the silver to bring about an equally smooth surface regardless of the grade of emery paper on which the silver was polished. At lower pressure or temperature, the adherence of the bond might be more noticeably affected, since lower pressure or temperature would not be so effective in causing flow of the silver and the resulting intimate contact.

Figure 1 is a photomicrograph showing silver strips bonded by heating to 400 °C and passing once through the rolls. The boundary line between the original surfaces can be seen to be of the same order of magnitude as the grain boundaries, indicating a strong bond.

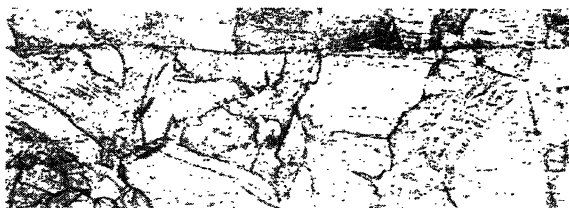


FIGURE 1. Two silver strips bonded (at A—A) by first heating to 400 °C and then passing once through steel rolls.  $\times 200$ .

In the experiments carried on in the pressure apparatus to be described later, in which the specimens were subjected to pressure while held at any desired temperature, it was found that the surface condition was more important. Silver strips polished only on No. 1 emery paper gave a bond of appreciably less adherence than those polished with finer grades. This difference was probably because the flow induced by rolling tended to make a more uniform surface than the flow when the position of the strips was fixed.

Attempts to bond silver-plated copper strips by rolling were unsuccessful because the application of heat and pressure caused the silver to diffuse into the copper to such an extent that there was not sufficient contact between the silver surfaces, these being replaced in part by oxidized copper.

Silver-plated steel was bonded by heating to 400 °C and rolling. The adherence of the silver to silver was greater than that of silver to steel, so that the plating separated from the steel when the strips were pulled apart.

### Effect of Temperature and Pressure

For quantitative measurements, an apparatus was constructed which applied heat and pressure simultaneously to the strips and permitted measurement of both. The strips to be welded were placed on a metal

base and pressure was applied from above by a system of levers. The device and specimen were housed in an electric resistance furnace by means of which the desired temperature could be obtained and indicated by a thermoelectric pyrometer. A weight was applied to one of the strips of silver at right angles to the applied pressure, thus inducing a tension on the strip. In this apparatus it was possible to obtain welds of which the adherence compared favorably with that obtained by rolling.

In the bonding experiments, the thickness of the lower silver strip seemed to be unimportant in determining the strength of the bond, but the thickness of the upper strip was very important. When the upper strip was greater than 0.3 mm in thickness adherent bonds were not obtained. This may be explained by considering the resistance of the heavier piece of silver to deformation. When the upper strip was thick, the applied pressure was not so effective in causing it to conform to the surface of the lower strip and so the area of contact was much less than when a light strip, which could easily be deformed, was used.

The strips to be used were polished successively on No. 1, No. 0, No. 00, and No. 000 emery paper and cleaned thoroughly with benzene to remove any foreign matter. They were then placed in the furnace, heated to the desired temperature, and the pressure applied.

It was difficult to establish a method for determining the strength of the weld, and it was finally decided to consider as an adherent weld one in which the upper strip of silver would tear away around the weld without separation of the strips in the area of applied pressure. Under this condition, the strength of the weld would be greater than the breaking (tearing) strength of the upper strip of silver.

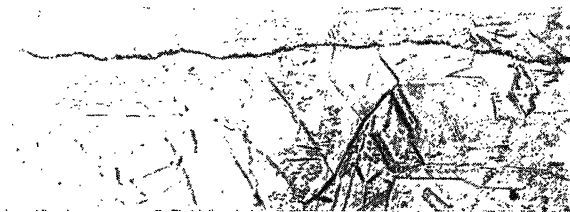


FIGURE 2. Two silver strips bonded (at A—A) at 400 °C and under a vertical pressure of 45,000 pounds per square inch maintained for  $\frac{1}{2}$  hour.  $\times 200$ .

Figure 2 is a photomicrograph of a weld obtained in the vertical-pressure apparatus at a temperature of 400 °C and under a pressure of 45,000 pounds per square inch applied for one-half hour. When compared with a weld obtained by rolling, it may be seen that the line of demarcation between the strips is wider. It is therefore apparent that the rolling operation, in which the pressure is not known, produced a stronger bonding

of the strips, although in both cases the bond was sufficiently strong to pass the test noted in the preceding paragraph.

Figure 3 shows the time necessary to obtain an adherent weld at different temperatures under pressures of 45,000 and 25,000 pounds per square inch. Although in many cases considerable adherence was obtained in less time than that shown on the curve, the strips could be separated without tearing the silver, and accordingly the surfaces were not regarded as being welded.

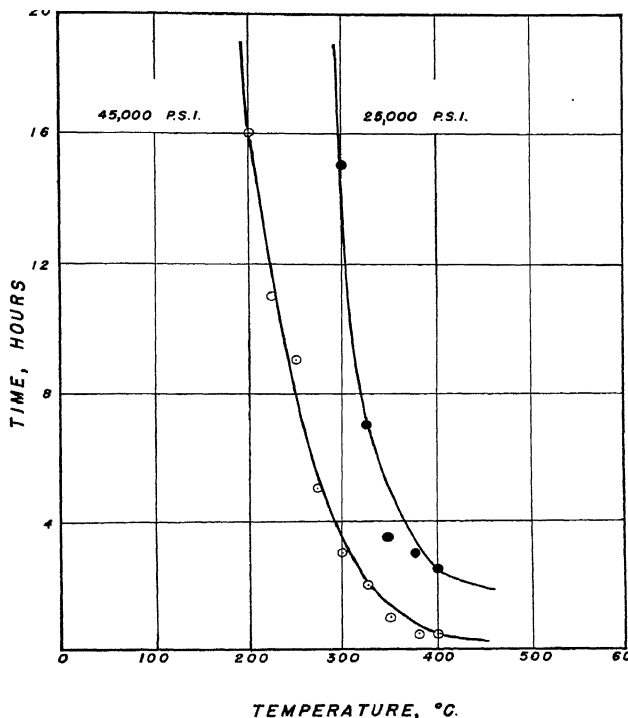


FIGURE 3. Time-temperature relationship necessary to produce adherent welds under pressures of 45,000 and 25,000 pounds per square inch.

At temperatures below 200 °C adherent welds were not obtained, although sticking was evident when the pressure was applied for fifty or sixty hours. Above 400 °C the silver became so soft that accurate measurements were not possible, because the application of pressure caused too great a flow of the silver.

In all the welded specimens there was a considerable flow of the metal,



a depression being made in the lower strip into which the upper one conformed. Table 1 shows the comparative combined thickness of the two plates before and after the welding operation. In all cases in which measurements were made, the thickness of an adherent weld was between 20 and 25 per cent of the original thickness of the two strips. The proce-

Table 1.—Thickness of the Combined Two Silver Plates Before and After Pressure Welding.

Pressure Applied— (lb/in <sup>2</sup> ) (kg/cm <sup>2</sup> )		Temp. (°C)	Time (hr)	Original Thickness (mm)	Thickness After Pressure Welding (mm)	Per Cent of Original Thickness
45,000	3,150	400	$\frac{1}{2}$	1.19	0.25	21.0
45,000	3,150	350	1	1.78	0.36	20.2
45,000	3,150	250	8	1.25	0.28	22.4
45,000	3,150	200	16	1.86	0.41	22.0
34,000	2,380	400	1	1.25	0.31	24.8
23,000	1,610	400	$5\frac{1}{2}$	1.16	0.28	24.1

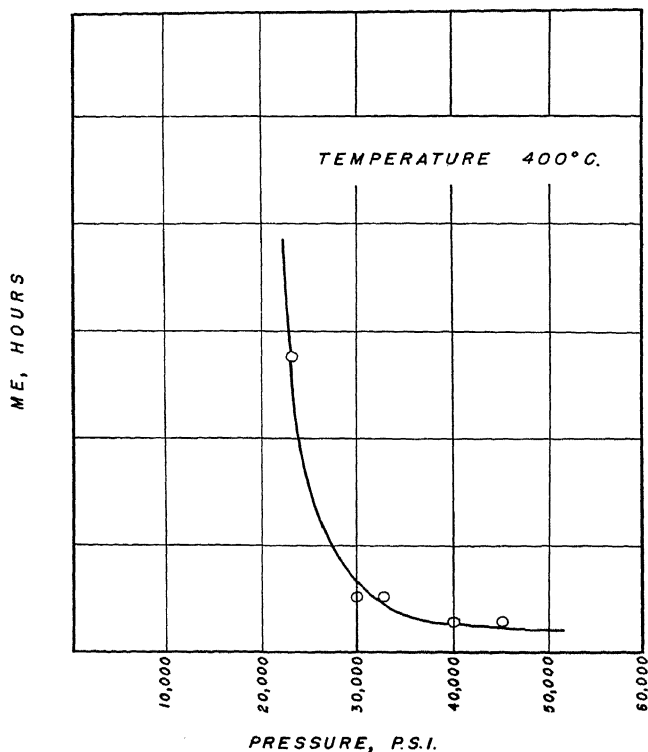


FIGURE 4. Change in time necessary to produce an adherent weld at constant temperature caused by a variation in pressure.

ture used in testing the adherence of the welds usually made it difficult to measure the thickness of a weld which was not adherent, but such measurements as were possible showed that the reduction in thickness varied greatly, in all cases being greater than 25 per cent.

Figure 4 shows the relationship between the pressure applied and the length of time necessary to obtain an adherent bond. This curve is of the same general form as those shown in Figure 3, which would suggest that temperature and pressure are of about equal importance in determining the bonding time.

### Effect of Preheating

In the experiments described above, the temperature at which the pressure was applied was the maximum temperature to which the silver was heated. Further experiments were carried on to determine the effect of preheating the silver to redness before the application of pressure at a lower temperature. The silver strips were heated to redness in a Bunsen flame and pressure applied when they had cooled to the desired temperature. The pressures used were much higher than in the previous experiments, and were applied for relatively short times of application. The pressures were obtained on a Brinell hardness tester equipped with a 5-mm ball.

The results of the tests performed with the Brinell machine are shown in Tables 2, 3, and 4. The method of rating the tests is given beneath each table. Tables 2 and 4 give the results of tests in which the silver was preheated to redness before the application of pressure, while Table 3 gives the results of tests in which the silver was welded at room temperature without any preheating. Spectroscopically pure silver was used in

Table 2.—Pressure Welding of Spectroscopically Pure Silver Sheet (0.5 mm Thick) after Preheating to Redness.

Load		Pressure (Calc.)		Time of	Temperature	Results*
(kg)	(lb)	(lb/in <sup>2</sup> )	(kg/cm <sup>2</sup> )	Application (sec)	When Welded (°C)	
1,500	3,300	100,000	7,000	30	Red heat	A
1,500	3,300	100,000	7,000	30	Approx. 70	A
1,500	3,300	100,000	7,000	30	Room temp.	AAAAA
1,000	2,200	70,000	4,950	30	Red heat	AA
1,000	2,200	70,000	4,950	30	Approx. 70	A
1,000	2,200	70,000	4,950	30	Room temp.	CAA
750	1,650	50,000	3,500	30	Red heat	AAA
750	1,650	50,000	3,500	60	Approx. 70	FF
750	1,650	50,000	3,500	30	Room temp.	CAFFC
500	1,100	40,000	2,800	45	Red heat	A
500	1,100	40,000	2,800	30	Red heat	AAAA
500	1,100	40,000	2,800	15	Red heat	AAA
500	1,100	40,000	2,800	60	Approx. 70	C
500	1,100	40,000	2,800	30	Approx. 70	C
500	1,100	40,000	2,800	60	Room temp.	FFF
500	1,100	40,000	2,800	30	Room temp.	FCFFF

\*Each letter represents the rating of a single test in which A = complete welding, C = partial welding, and F = no welding.

the tests reported in Tables 2 and 3 while 999.3 fine silver was used for the tests reported in Table 4.

A comparison of Table 2 and Table 3 shows the effect of heating the silver to red heat before application of pressure. If the silver had been previously heated, complete welds were obtained with a pressure of 70,000 pounds per square inch applied for 30 seconds, while without the heat treatment, as shown in Table 3, no welds were obtained under these conditions. At 100,000 pounds per square inch for a similar length of time, all good welds were obtained when the silver had been heated before the pressure application. Under similar conditions, silver without preheating did not give consistently good welds even when the pressure was applied for two and one-half minutes.

Table 3.—Pressure Welding of Spectroscopically Pure Silver Sheet (0.5 mm Thick) at Room Temperature, not Preheated.

(kg)	-Load- (lb)	-Pressure (Calc)-		Time of Application of Pressure (sec)	Results*
		(lb/in <sup>2</sup> )	(kg/cm <sup>2</sup> )		
3,000	6,600	193,000	13,510	30	AA
2,500	5,500	160,000	11,200	30	A
2,000	4,400	130,000	9,100	30	A
1,500	3,300	100,000	7,000	150	AAAF
1,500	3,300	100,000	7,000	120	FAAFF
1,500	3,300	100,000	7,000	90	FF
1,500	3,300	100,000	7,000	60	AFCFCA
1,500	3,300	100,000	7,000	60	FCACAC
1,500	3,300	100,000	7,000	45	A
1,500	3,300	100,000	7,000	30	FFCFAAAA
1,500	3,300	100,000	7,000	30	CFACAC
1,000	2,200	70,000	4,950	150	F
1,000	2,200	70,000	4,950	120	FCFC
1,000	2,200	70,000	4,950	90	CCF
1,000	2,200	70,000	4,950	60	F
1,000	2,200	70,000	4,950	30	F

\*Each letter represents the rating of a single test in which A = complete welding, C = partial welding, and F = no welding.

Table I also indicates that complete welds of silver to silver can be obtained with pressures as low as 40,000 pounds per square inch at temperatures approaching red heat in as short a time as fifteen seconds. From the curves obtained with the vertical-pressure apparatus (Figures 1 and 2), in which no preheating was used, it did not appear that such a result would be expected. On the other hand, the data of Table 3, while all in a higher pressure range than used in the other apparatus and therefore not closely comparable, are not inconsistent with those results.

### Effect of Purity

Table 4 presents data obtained with 999.3 fine silver instead of spectroscopically pure silver, employing the preheating treatment as in the case of Table 2. Although the results shown were obtained using a 5-mm ball in the Brinell machine, a considerable number of welds were

Table 4.—Pressure Welding of Silver Sheet 999.3 Fine (0.75 mm Thick) after Preheating to Redness.

(kg)	(lb)	Pressure (Cale)- (lb in <sup>2</sup> )	(kg cm <sup>-2</sup> )	Time of Application (sec)	Temperature When Welded (°C)	Results*
1,500	3,300	140,000	9,800	30	Red heat	A
1,500	3,300	140,000	9,800	30	Approx. 70	AAA
1,500	3,300	140,000	9,800	60	Room temp.	AA
1,500	3,300	140,000	9,800	30	Room temp.	A
1,000	2,200	100,000	7,000	30	Red heat	AA
1,000	2,200	100,000	7,000	30	Approx. 70	FFF
1,000	2,200	100,000	7,000	60	Room temp.	AAAAAAA
1,000	2,200	100,000	7,000	30	Room temp.	FFC
750	1,650	75,000	5,250	30	Red heat	AAA
750	1,650	75,000	5,250	60	Approx. 70	AA
750	1,650	75,000	5,250	30	Approx. 70	FFC
750	1,650	75,000	5,250	60	Room temp.	AAAFCCAAC
750	1,650	75,000	5,250	30	Room temp.	FF
500	1,100	50,000	3,500	30	Red heat	FAC
500	1,100	50,000	3,500	60	Approx. 70	FF
500	1,100	50,000	3,500	30	Approx. 70	F
500	1,100	50,000	3,500	60	Room temp.	F
500	1,100	50,000	3,500	30	Room temp.	F

\*Each letter represents the rating of a single test in which A = complete welding, C = partial welding, and F = no welding.

also made using a 10-mm ball. The results were not different from those tabulated.

A comparison of Table 2 with Table 4 indicates that only a slight improvement in weldability is gained by using spectroscopically pure silver as compared with 999.3 fine silver. It can be seen that good welds were obtained consistently with spectroscopically pure silver at red heat under a pressure of 40,000 pounds per square inch applied for thirty seconds, while only one good weld was obtained with 999.3 fine silver at red heat under a pressure of 50,000 pounds per square inch applied for thirty seconds. However, no such striking differences are seen in comparing Table 4 with Table 2 as in comparing Table 3 with Table 2.

Some of the data in Table 4 are in the same pressure ranges as covered by the curves referred to earlier. The conditions were similar in that no preheating was used, but differ as regards the apparatus used. The data of Table 4 are consistent with those previously obtained.

### Effect of Films of Foreign Matter

To determine the effect on the welding and find what sort of film would most effectively lessen sticking of silver to silver when this is not desirable, films of foreign material were introduced between the silver strips to be welded in the vertical-pressure apparatus. The adherence of strips polished successively on all four grades of emery paper from No. 1 to No. 000 was taken as a basis for comparison. In most instances the film was not uniform and calculation of the thickness could not be made. In those cases where there was no visible discontinuity of the film, an estimate of the average thickness was calculated from the weight of the film,

the area, and the density of the material. The averages obtained are as follows:

Iron oxide .....	0.00026 mm
Aluminum powder .....	0.00133 mm
Aluminum oxide .....	0.00032 mm
Zinc oxide .....	0.00034 mm

Under a microscope, however, it could be seen that even these films consisted of spacially separated particles.

Somewhat surprisingly, the presence of these films, as well as of very thin films of powdered copper, copper oxide, silver oxide, silver sulfide, charcoal, petroleum jelly, mineral oil, and lubricating grease, did not materially lessen the strength of the bond. Graphite and talc were slightly more effective than the other films in lessening the adherence of the bond, talc being more effective than graphite. The talc, however, was more difficult to apply than the graphite and appeared to give a heavier coating.

Although the presence of foreign matter would be expected to cause a decrease in adherence, the films used were thin and probably had considerable areas of discontinuity, which may be the reason that welding was not prevented. Studies in the adherence of electroplatings have consistently demonstrated the importance of absolute cleanliness, but there the factors of pressure and plastic flow are absent. It may be that the importance of foreign matter has been over-emphasized in pressure welding, where the continuity of the film may be destroyed in the process and an opportunity presented for welding around the particles of foreign matter. In the case of oil and grease, instability of the film at elevated temperatures was probably a factor.

E. G. West, in a discussion of this work, has observed that in the application of pressure alone, the inter-atomic distances are too great, except at a few points on the surface, for complete adhesion to be obtained; at the points of true contact, however, the pressure will rise to very considerable values, causing break-down of surface films, if present, and probably the development of local high-temperature areas. Plasticity is thus increased considerably, increasing the chances for atomic forces to become effective. Slight motion will assist the rupture of surface films, while higher temperatures increase plastic flow.

### **Cold-welding of Gold**

Some comparative tests were made in welding gold sheet under pressure in a Brinell machine both with and without preheating in a Bunsen flame. The gold used was 0.25 mm in thickness and was 999.85 fine. It was found possible to obtain a complete weld between two strips of gold previously heated to redness, when a pressure of 45,000 pounds per square inch was applied for 30 seconds at room temperature. Although the minimum pressure for welding was not determined, it was evidently much below 45,000 pounds per square inch. Comparative tests with gold not preheated to redness showed that, just as with silver, a much higher

pressure is then necessary to get a complete weld. A good weld of gold sheet not preheated was obtained at 90,000 pounds per square inch in 30 seconds, while failures to weld were recorded at 78,000 pounds per square inch in 30 seconds. Although the number of tests made was insufficient for conclusive data, the pressures are considerably lower than were necessary for cold-welding of silver, especially in the case of the preheated material.

Two papers<sup>9, 10</sup> published by The Electrochemical Society give an account of this work in greater detail.

#### WELDING OF SILVER POWDER

The bonding properties of silver make it especially adaptable to utilization in the growing industrial application of powder metallurgy. Since the compacting of metallic powders involves a particle-to-particle bonding for a successful result, the principles discussed in this chapter apply in large measure to this process. However, the welding of innumerable surfaces of random distribution introduces complications which do not exist in the consideration of the bonding of two surfaces in contact. Numerous publications, of which two may be noted here,<sup>11, 12</sup> have discussed this question. The actual pressure existing at any individual surface contact in powder compression cannot be accurately determined. Variation in particle size, both in average and in distribution, is of great importance. For the best result, each particle should be made to conform exactly to its neighbors and become welded at every part of its surface. The presence of impurities and of adsorbed gas becomes of relatively greater importance, and there may be great difficulty in the escape of adsorbed gas. In practice, results vary with the actual method of effecting the welding—whether it is done after a previous sintering, whether the powders are alternately pressed to cause deformation and heated to produce recrystallization, or whether heat and pressure are applied simultaneously.

#### THE USES OF SILVER POWDER \*

The use of silver in powdered form is not new, but with the wide interest that is now being taken in powder metallurgy the question arises as to what extent this process may affect the consumption of silver.

Small amounts of silver powder have long been used to coat the surface of watch and clock dials. A paste is made containing salt, a small amount of tartaric acid and silver powder. This is brushed over the dial and a white deposit of silver is obtained. This particular use for silver is not important as far as the amount consumed is concerned, but when properly applied, the powder produces a beautiful white surface that cannot be duplicated by any other metal.

Another minor use for silver powder is the ornamentation of glass. Fine silver powder is mixed with borate of lead and lavender oil. This

\* This section has been prepared by Robert H. Leach, Vice-President of Handy & Harman.

paste is brushed on the surface of the glass to cover any design that may be desired. After drying, the article is then heated until the mixture fuses to the glass. If the article is then placed in a standard silver cyanide plating bath, any desired thickness of silver can be plated on that portion to which the silver paste has been applied. Beautiful designs on glassware can be made in this manner.

It is possible that considerable use for silver powder may be found in the electrical industry. The rapid development in this field is bringing a constantly increasing demand for better contact materials for use in making the different types of switches and circuit breakers. Fine silver and silver alloys that can be made by conventional methods of casting and fabricating are extensively used, but by means of powder metallurgy, it is possible to produce contact materials containing silver with varying percentages of some refractory metal or material which may perform better under certain types of severe service.

Silver and nickel do not alloy except in limited proportions, but it is possible to produce pressed and sintered products by using powders of these metals in any desired proportion. The fine silver and nickel powders are first mixed thoroughly in a mill until a uniform product is obtained. This mixture of powders is then placed in a mold of suitable size and either hot- or cold-pressed. The resulting pressed billet is then sintered at a temperature slightly below the melting point of silver. Repeated sintering and pressing or some other form of mechanical working can be carried on until the mixture practically reaches the density that would be expected from the combined metals if actually alloyed. On the other hand, if it is desired to do so, a uniformly porous product can be made by mixing some ingredient in the mass that can be volatilized after the pressing is done.

Graphite, tungsten, molybdenum and tantalum can be mixed with silver by this powder metal process and made into forms that can be used for electrical contacts or welding electrodes.

Some of these compositions can be rolled into thin sheet after being pressed and sintered a sufficient number of times, and this sheet can then be cut into proper-sized pieces for electrical contacts.

It is difficult to say to what extent this development will actually increase the use of silver because in many cases it is possible that some of these contact materials made from powdered silver and refractory metals will contain only 50 per cent or less of silver and will replace fine silver or silver alloys of much higher fineness. It is, however, an interesting development, because even wire suitable for use on a heading machine can be made from many combinations of metals that cannot be alloyed by conventional methods.

Coins or medals can be made from powdered silver instead of the usual melting, rolling, blanking and embossing methods, but in this case it is a question of relative economy of the different processes unless it is desired to use some refractory metal with silver.

## Chapter 7

### High-Temperature Bonding of Silver

By R. H. LEACH \*

Silver alloys have been used to join or bond metals for many centuries, but it is only in recent years that their use has expanded to the point where large quantities are consumed annually for this purpose in the arts and industries. The growth of the silverware and jewelry industry only accounts for a relatively small part of the increased consumption and it is in those industries devoted to the production of equipment and articles from sheet, tubing and wire that the greatest gains have been made.

Although the group of alloys commonly known as silver solders constitutes the largest volume, pure silver is used to some extent as a bonding material in the manufacture of chemical equipment. The base metals used in silver solders make them less resistant to some corrosive conditions than pure silver, and the most satisfactory method of resisting such corrosion is to use pure silver welding rods.

For convenience in describing the different uses of silver and silver alloys for joining metals the following divisions are based upon their melting temperatures.

1. Pure silver and silver alloys having melting points above 1600 °F.
2. Silver alloys having melting points from 1175 °F to 1600 °F.
3. Silver alloys having melting points below 1175 °F.

#### GROUP 1

Pure silver, or fine silver as it is called in the trade, melts at 1763 °F, and considerable skill is required to make satisfactory joints with it on silver or silver-clad base metals. The heat conductivity of silver is very high and, when molten, silver absorbs a large amount of oxygen when exposed to the air. These two factors make it necessary to provide a method of rapid heating and to protect the joint from an oxidizing atmosphere during the welding. If the members are preheated for a considerable distance away from the joint and the atomic hydrogen arc is used for melting the fine silver welding rod, it is possible to secure a good bond between fine silver sheets or tubing. When silver-clad iron or nickel are joined with fine silver rod it is necessary to exercise great care to prevent contaminating the silver with the base metal. Fortunately

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iron does not alloy with silver, and nickel alloys only to a limited extent; and as both metals melt at temperatures several hundred degrees above the melting point of silver, a skilled workman has a sufficient margin of safety to do a good job. Figure 1 shows a joint made with silver welding rod on silver-clad steel, and Figure 2 is an autoclave with silver lining and cover. In some instances a small amount of another metal has been

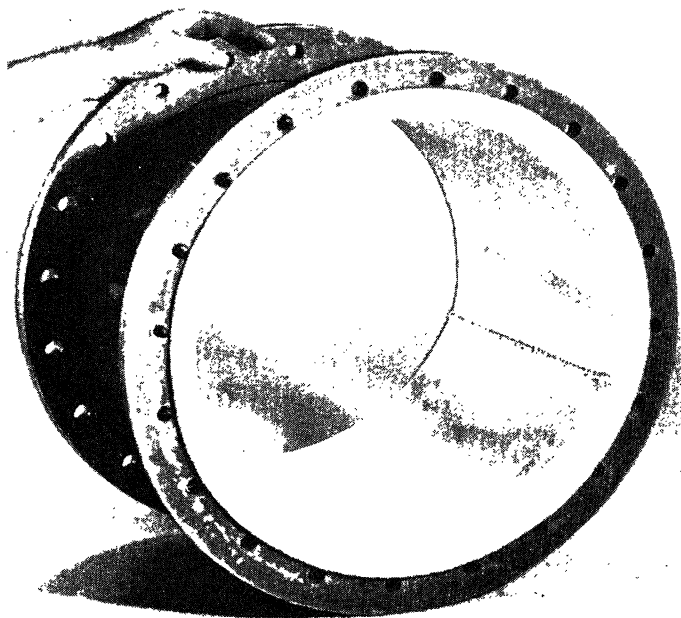


FIGURE 1. Section of silver-clad steel column.

added to fine silver, but the amount is not sufficient to lower the melting point materially, and the procedure to be followed would be similar to that with fine silver. Welding with fine silver rod can also be done with oxyacetylene torches by using one torch ahead of the other, in order to do the preheating necessary to take care of the losses from high heat conductivity of the material. When preheating is done in this manner the expansion of the sheets occurs principally under the first torch, and it is therefore possible to keep them in better alignment under the welding torch.

Alloys consisting of copper with small additions of silver are used for welding copper sheets. The Canzler patent, which expired several years

ago, was based upon the claim that the addition of silver in amounts up to 5 per cent and a small proportion of phosphorus made an excellent rod for joining copper sheet and tube. The amount of silver and phosphorus present in commercial rods of this type is not sufficient to lower the melting point to any considerable degree, but reports from the field indicate that better joining can be obtained. The liquidus, or flow point, of a brazing alloy is not the only characteristic to be considered, because



FIGURE 2. Silver autoclave with silver lining and cover.  
(Fine silver fabrication).

two alloys having the same liquidus point may not flow equally well, either because of a difference in the actual fluidity or because of a difference in their wetting properties on the surfaces of the joint. There seems to be sufficient evidence to justify the statement that silver in small quantities does improve the properties of certain types of welding rods, although the melting temperature is not lowered in the same degree that is obtained in the alloys of the second group. A number of copper-base alloys containing silver and either tin or manganese have melting points from 1700 to 1800 °F. These alloys have quite different properties from those of the common base metal welding rods that melt at the same temperature, and are therefore more suitable for some applications.

## GROUP 2

We now come to the second and most important group of silver alloys that are used for joining metals. These alloys require a temperature above a dull red, or approximately 1000 °F, to melt them; they have been called silver solders for many years. The wide use of tin-lead alloys or soft solders in industrial fields has created the impression in many minds that the term solder or soldered joints refers to alloys of this type and joints made with them. To eliminate any confusion the change in name from silver solders to silver brazing alloys has been suggested, and this term is being used to considerable extent. The procedures followed in using these silver alloys are similar to those used with base metal brazing alloys or spelters, and joints made with them are of equal or greater strength than those made with the base metal alloys.

The silver brazing alloys include a wide range of compositions containing from 5 to 80 per cent silver. Many years ago metal workers found that the addition of silver to brass produces an alloy having a considerably lower melting point than the brass, and at the same time makes exceptionally strong joints when used for brazing. Many silver solders are therefore composed of silver, copper and zinc, and a number of the old formulas specified a given number of parts of silver and of brass. Small proportions of tin, cadmium, nickel, manganese are also used in some of the compositions. Table 1 gives the standard list of silver solders that was adopted in 1929 by the American Society for Testing Materials.

Table 1.

Grade No.	Silver (%)	Copper (%)	Zinc (%)	Cadmium (%)	Impurities (Max. %)	Melt. Point (°F)	Flow Point (°F)	Color
1	10	52	38	a	0.15	1510	1600	yellow
2	20	45	35	a	0.15	1430	1500	yellow
3	20	45	30	5	0.15	1430	1500	yellow
4	45	30	25	nil	0.15	1250	1370	nearly white
5	50	34	16	nil	0.15	1280	1425	nearly white
6	65	20	15	nil	0.15	1280	1325	white
7	70	20	10	nil	0.15	1335	1390	white
8	80	16	4	nil	0.15	1360	1460	white

\* The addition, not to exceed 0.50 per cent of cadmium to assist in fabricating Grades No. 1 and 2, shall not be considered as a harmful impurity.

The table gives the melting point or solidus and flow point or liquidus of each alloy, but in practice the latter generally is referred to as the melting point as it is the lowest temperature at which the alloy is entirely fluid and can be used satisfactorily. Other ternary alloys of silver, copper and zinc can be used. Figure 3 is a diagram which shows the temperature at which different compositions become entirely liquid.

The silver-copper eutectic which melts at 1435 °F is used as a brazing alloy in those cases where zinc or cadmium would be harmful. There are

two proprietary alloys, one of which melts at 1175 °F and contains silver-copper-zinc and cadmium; the other melts at 1300 °F and is composed of silver, copper and phosphorus. These alloys have a wide commercial application, the former being used on both ferrous and non-ferrous metals and alloys and the latter on non-ferrous.

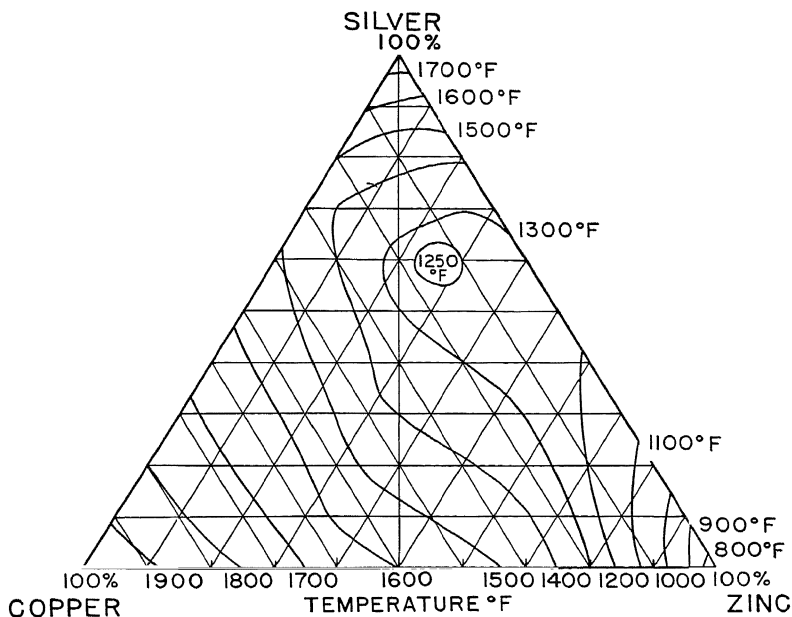


FIGURE 3. Liquidus diagram of silver-copper-zinc alloys.

Alloys can be made containing one or more of the metals tin, manganese and nickel with silver and copper; these have melting points within the range of those of the standard silver solders.

### Properties of Silver Brazing Alloys

Among the most important properties that make these alloys so valuable to industry are: low melting points, malleability and ductility, high strength of joints made with them, corrosion resistance and electrical conductivity.

#### Low Melting Points

Because these alloys have lower melting points than base metal brazing alloys, which melt at temperatures above 1600 °F, the time required to make a joint is much less and a much greater margin of safety from

damage by overheating is provided. Many of the non-ferrous alloys which have been developed in recent years may be seriously affected by the higher temperature required for base metal brazing alloys, and this is particularly true when joining thin sheets or tubing.

### Malleability and Ductility

These alloys can be rolled into thin sheet or strip and drawn into wire of small diameter. It is thus possible to provide the brazing alloy in that form and size which will be most convenient and economical for any specific application. The strongest silver brazed joints are those which have only a few thousandths of the alloy as a bonding material; placing thin inserts of the alloy in the joint before heating is a most satisfactory way of applying them. Narrow strips or different sizes of wire can be used when the alloy is fed into the joint, and a workman can select the size of strip or wire which is most convenient and will therefore be able to make neat joints quickly without wasting the alloy. The advantage of being able to use small sizes of wire is particularly important where small parts are to be joined. The ductility of the wire allows rings to be made for preplacing in the joint, and other forms can be easily supplied. Regardless of the form in which the alloy is used it has the cast structure after the joint is cooled; and because these alloys are malleable and ductile as cast, those properties are imparted to the joint.

### Strength of Joints

Joints made with silver brazing alloys are strong and highly resistant to shock and vibration. Butt, scarf and lap joints are suitable, and it is desirable to use care in fitting the members in order that the clearances will be small and the greatest strength obtained. Scarf and lap joints allow a greater factor of safety because a larger surface area of joint can be provided.

The actual strength of joint will depend upon the metals joined and types of joint; but with proper design there is no difficulty in getting strengths equal to or greater than those of the metals of the different members. Table 2 gives a concrete example of the strength of some test joints that were made on Everdur.

Table 2.—Relative Strength of Butt and Lap Joints Made with a Silver Brazing Alloy on  $0.080 \times \frac{1}{8}$ " Everdur Strip.

No.	Type of Joint	Tensile Strength (lbs. per sq. in.)	Elongatic in 2 inc.
	Stock as received	60,900	51.5
1	$\frac{3}{8}$ -inch lap	57,400	43.7
2	$\frac{1}{2}$ -inch lap	56,200	43.7
3	$\frac{5}{8}$ -inch lap	56,900	50.0
4	$\frac{3}{4}$ -inch lap	57,300	50.0
5	$\frac{7}{8}$ -inch lap	57,200	50.0
6	Butt	57,200	50.0

The figures given in Table 2 show the relative strength of different lap joints as compared with butt joints on the same material. All of the specimens broke in the Everdur outside of the joint. These test specimens were made by applying a light pressure to the members to hold the joint surfaces in close contact in both the lap and butt joints.

The strength of the silver brazing alloys is often questioned. Although it is the strength of the joint rather than that of the brazing alloy that is important, these alloys in general have a tensile strength from 40,000 to 60,000 pounds per square inch in cast form. In those joints, therefore, where the alloy is actually used as a filler and there is a considerable space between the parts after brazing, these figures are indicative of what strength may be expected in the butt joints.

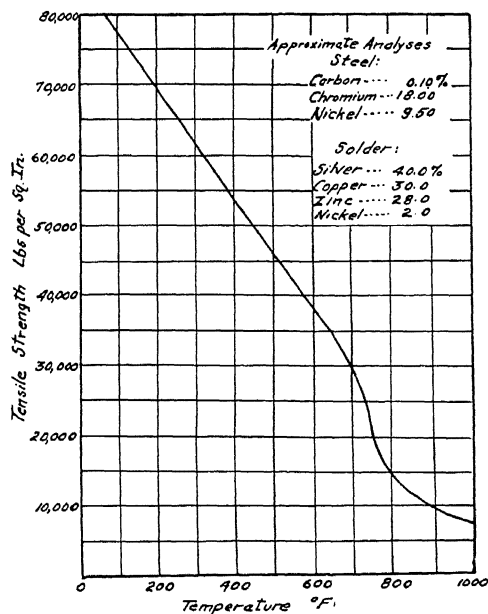


FIGURE 4. Effect of temperature on strength of silver-soldered stainless steel joints.

The strength of a joint made with these alloys is affected by high temperatures. Figure 4 gives the results of some short-time tests that were made on stainless steel which had been joined with a silver brazing alloy. It is evident from the diagram that the strength of the joint is greatly reduced at temperatures above 700 °F. Tests on high-pressure steam lines indicate that 450° F is about the limit of temperature to

which joints made with silver brazing alloys should be subjected and provide a reasonable factor of safety for such severe service.

### **Corrosion Resistance**

Silver brazing alloys are resistant to the ordinary types of corrosion for which brass, copper, nickel silver and cupro-nickel alloys are used. A wide range of compositions can be obtained by varying the base metal components, and it is thus possible to select alloys to meet special conditions. For example, a very satisfactory silver-zinc alloy has been developed for use in those applications where the presence of copper would be harmful. Alloys containing silver and copper, such as the silver-copper eutectic previously mentioned; silver-copper-manganese and silver-copper-manganese and nickel can be used to meet those conditions where zinc or cadmium would be harmful.

The thin section of alloy that is present in a properly designed joint is an important advantage because the surface area exposed to the corrosive attack is extremely small. Strong lap joints can be made on sheet metal with such a thin layer of the alloy that even though the alloy may corrode more rapidly than the metal, exposure is so much less that the joint will not fail until the metal itself has been corroded beyond its usefulness.

Galvanic corrosion of brazed joints is always an important point to consider; and as this type of corrosion is proportional to the exposed areas the advantage of using a cathodic joining alloy is obvious. Silver brazing alloys containing relatively high percentages of silver are noble to many metals under highly corrosive conditions and are, therefore, most useful as a joining medium. Monel metal and the iron-chromium-nickel alloys are typical examples to which these silver alloys are cathodic in many corrosive conditions. In the case of nitric acid solutions the reverse is true and silver alloys should not be used.

### **Electrical Conductivity**

The conductivity of silver brazing alloys varies considerably, but alloys having high silver content can be made that have from 50 to 75 per cent of the conductivity of copper. They are extensively used in the electrical industry. An excellent paper by Reed and Edelson<sup>8</sup> gives detailed information regarding joints made with them on transformers and other electrical equipment.

### **Procedures for Using Silver Brazing Alloys**

It is easy to make good joints with these alloys but a few points are important to keep in mind.

#### **Design**

It is wasteful to use silver alloys as fillers or on V joints because they flow freely into narrow openings and the strongest joints are

obtained with small clearances. Figure 5 illustrates several types of joints.

Preplacement of the alloys offers many advantages such as: the amount used can be controlled, thus preventing waste; the workman can give his entire attention to proper heating if a torch is used; the appearance of the alloy at the edge of the joint is a good indication that the joint has been heated to the proper temperature; when thin inserts of the alloy are used between flat members a pressure can be applied and uniform wetting of the surfaces assured. Regardless of whether the alloys are preplaced or hand fed, the designer should whenever possible restrict the clearances between members to a maximum of a few thousandths of an inch. Figure 6 gives the results of some tests which illustrate the relative strength with different clearances. It will be noted that the maximum strength was obtained with a clearance of approximately  $1\frac{1}{2}$  thousandths of an inch. Further details regarding design are given in a paper by Leach and Edelson.<sup>13</sup>

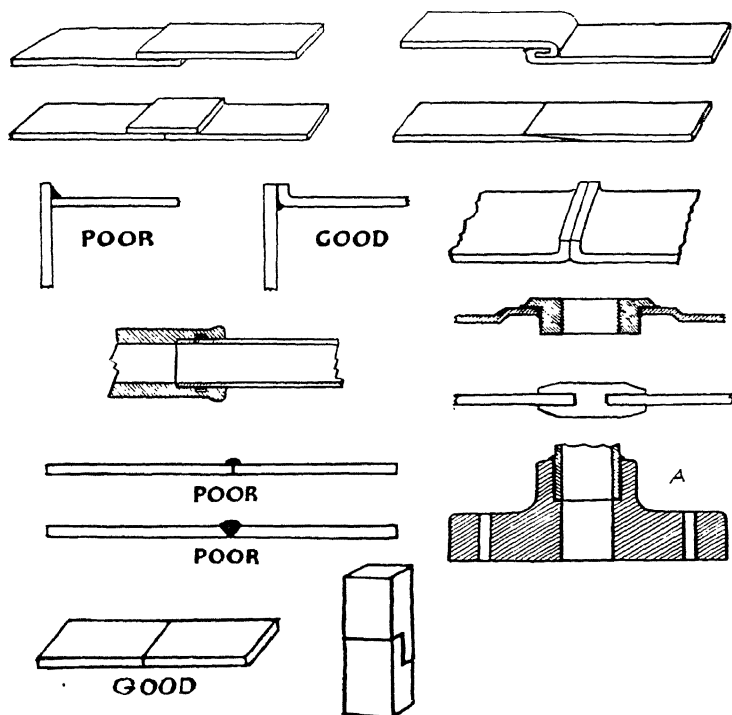


FIGURE 5. Types of joints made with silver brazing alloys.



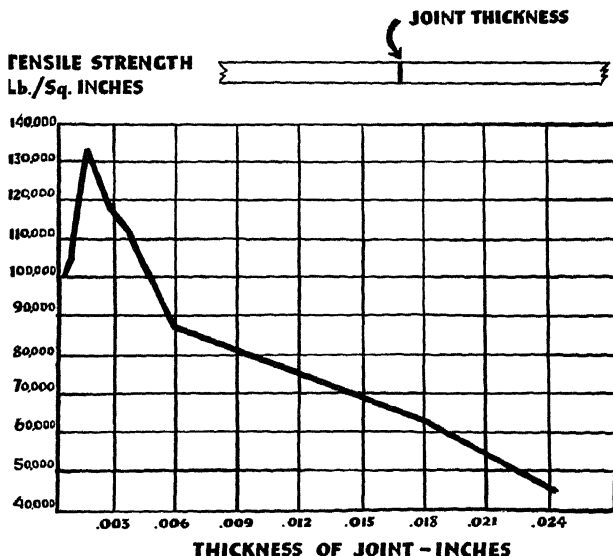


FIGURE 6. The relation of joint thickness to tensile strength. Chart based on butt joints, stainless steel to stainless steel.

### Cleaning

It is necessary to have all surfaces of the joint clean and free from scale, grease and dirt. Mechanical or chemical methods may be used. Careful attention to this item is one of the most important factors in obtaining satisfactory results, and field experience has shown that lack of attention to this detail is often the cause of faulty joints.

### Fluxing

Even when the heating is done in a reducing atmosphere the use of a small amount of flux is often helpful, and in all other cases it is imperative. The only exception is when a silver brazing alloy contains a sufficient amount of phosphorus and is used in joining copper to copper.

The flux has three functions: to prevent oxidation of the surfaces and the brazing alloy, to dissolve any oxides that may form, and to assist the free flowing of the brazing alloy. The flux must be fluid and active at the brazing temperature. Borax and combinations of borax and boric acid have been standard fluxes for brazing work for many years.

However, silver brazing alloys having melting points below the temperature at which borax is a thin fluid require a different flux; the best results are obtained when full advantage is taken of their low melting points. A proprietary flux which is not viscous at temperatures above 1020 °F is widely used. Fluxes containing the alkaline bifluorides give

best results with stainless steels or other metals or alloys that have refractory oxides. The proprietary flux just mentioned is also particularly good for this purpose.

### Jigging

The members must be properly supported during heating to keep them at the correct relative positions and the assembly should be allowed to cool until the brazing alloy has solidified before removing any wires or jigs.

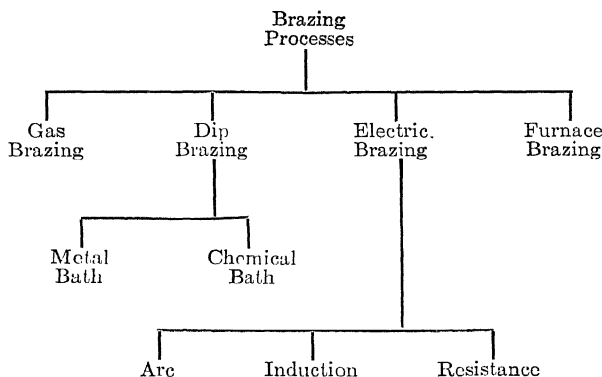


FIGURE 7. Different forms of heating.

### Heating

The different forms of heating that may be applied are illustrated in Figure 7. This is a brazing process chart adopted by The American Welding Society and all of the methods shown in that chart can be used with silver brazing alloys.

Heating by some type of torch is the method most widely used. The ordinary gas and air torch may be used with city gas, natural gas or some of the bottle gases such as propane or butane. Oxygen-gas, oxyhydrogen and oxyacetylene torches are also used. The oxyacetylene torch has been developed to a high degree of perfection and it can be regulated easily so that either a neutral or a slightly reducing flame can be maintained. At the same time, because of its high temperature, the maximum flexibility and speed are provided with this torch. For small parts the air-gas torch is satisfactory, but with larger joints the tendency is to run this torch with an oxidizing flame. The greater speed and flexibility of the oxyacetylene torch make it more satisfactory in the majority of applications.

Torches with multiflame tips have also increased the efficiency and this speeds up production. When heavy parts are to be joined two flame



FIGURE 8. Silver alloy brazing with small two-flame torch.

torches using large tips are available. Figures 8 and 9 show how the torches are used.

Furnace heating can be used to advantage when there are a large number of small parts of uniform size to be brazed and also for heating large assemblies if they can be properly jugged. A reducing atmosphere should be used in the furnace.

Chemical baths give a quick method of heating and allow an accurate control of the temperature. This method can be used only when the type of joint is such as to allow the brazing alloy to be preplaced so that it will flow properly into the joint.

The metal bath is particularly suitable for joining the small wires. The ends of the wires are twisted or clamped together and are dipped into a small bath of the molten alloy.

### Electric Brazing

There are three types of electric brazing: arc, induction and resistance. *Arc:* The electric arc is used only to a limited extent for silver alloy

brazing, but it has been used to repair heavy non-ferrous castings when the alloy is used as a filler metal.

*Induction:* Induction heating provides a uniform and easily controlled method. It is necessary to preplace the brazing alloy, but the heating can be restricted to limited areas and the necessary temperature at the joint is produced quickly.

*Resistance:* One form of resistance brazing, called Incandescent Carbon, is a method in which the heat is generated in carbon electrodes. Convenient portable equipment is manufactured in which these carbons are held in tongs; this method affords an excellent means for making lap joints on small flat strips. The alloy is preplaced in the joint and as a slight pressure can be applied by means of the tongs a good bond is assured. A paper on incandescent carbon brazing by Reed and Edelson<sup>8</sup> gives further details in regards to the use of this method. Incandescent carbon brazing and other electrical resistance types have several advantages. The heating is rapid and easy to control. It can be confined to a small area and in some cases the pressure holds the parts in place and jigs are not required.

The selection of the best method of heating will depend upon many

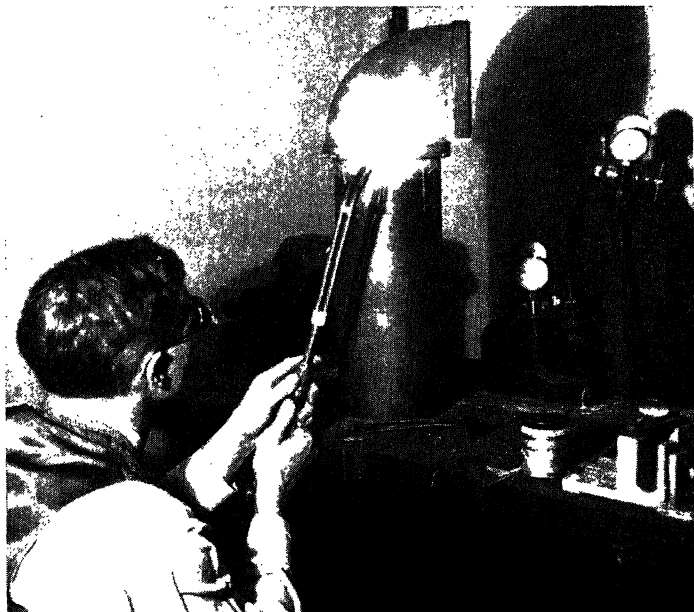


FIGURE 9. Large two-flame torch for silver brazing large flange assembly.

different factors, but in any case it is important that the heat be controlled carefully to take advantage of the low temperature at which these silver brazing alloys melt.

### Typical Uses of Silver Brazing Alloys

Large quantities of these alloys are used in the manufacture of different types of refrigeration equipment. Strong, leak-proof and corrosion-resistant joints can be made quickly with all the metals used in the manufacture of this equipment with the exception of aluminum or alloys which melt below a temperature of 1250 °F. Figure 10 shows a condenser for a household refrigerator which is brazed with a silver alloy.

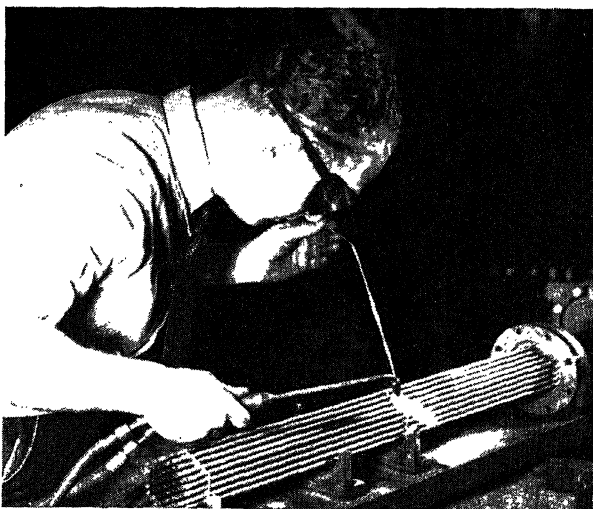


FIGURE 10. Silver alloy brazing small condenser for household refrigerator.

Air conditioning equipment and installations are other applications where these alloys have replaced soft solders because of their greater strength and the corrosion resistance of the joints.

The electrical industry is another large user of these alloys. Figure 11 is a transformer which has 400 joints that have been made with a silver brazing alloy and the squirrel-cage rotor shown in Figure 12 has 96 joints. Bus bar assemblies and joints on all kinds of electrical equipment are now being made with silver brazing alloys. Strong joints between dissimilar metals can be made with these alloys. Figure 13 shows an oil float with a steel body and a brass tube.

A very interesting application is shown in Figure 14. This is a water-tube boiler which is brazed with a silver alloy which melts at 1175 °F. The mild steel headers of the boiler are  $\frac{3}{4}$ " thick and 48" in diameter; 1238 copper tubes  $35\frac{1}{2}$ " long,  $\frac{3}{4}$ " OD  $\times$  0.049" wall thickness were brazed to this header in an electrically heated furnace. This boiler is operated at 225 pounds per square inch pressure, the temperature of the steam

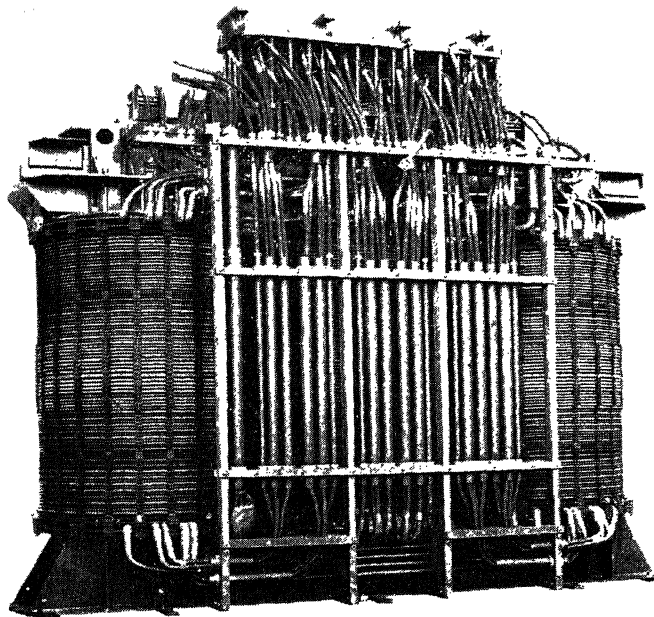


FIGURE 11. Transformer having 400 joints made with silver brazing alloy.

being 395 °F, and the service is satisfactory. More complete details of the construction of this boiler may be found in a paper by Weir and Webber.<sup>7</sup> It is an excellent illustration of what can be done with low-temperature silver brazing alloys.

The use of silver alloys for joining both iron and non-ferrous piping and tubing to fittings is increasing. Special fittings with rings of the alloy inserted in grooves cut in the fittings are available for standard pipe sizes as large as 10" in diameter, and flange joints as large as 42" in diameter are being made. This type of joint is specified for a large amount of the marine and navy piping and for buildings where the highest quality work is required. It is believed that further expansion in this

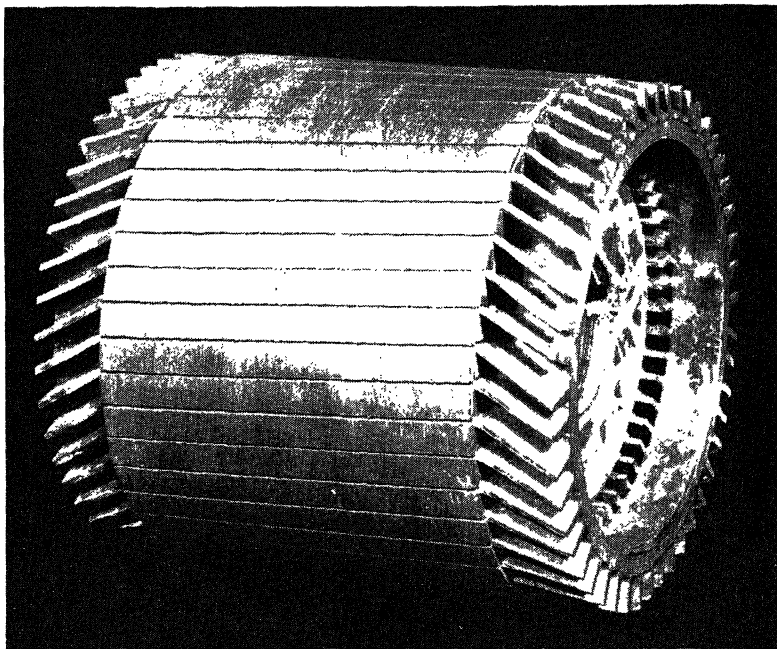


FIGURE 12. Squirrel-cage rotor with 96 silver alloy brazed joints.



FIGURE 13. Brass tube brazed to steel body of oil float with silver brazing alloy.

field will consume large quantities of these alloys because of the superiority of the silver alloy brazed joints over the standard threaded type. Figure 15 shows two installations of piping made in this manner that have been in use for several years. The following test illustrates the strength and resistance to shock that may be expected when pipe assemblies are brazed with silver alloys.

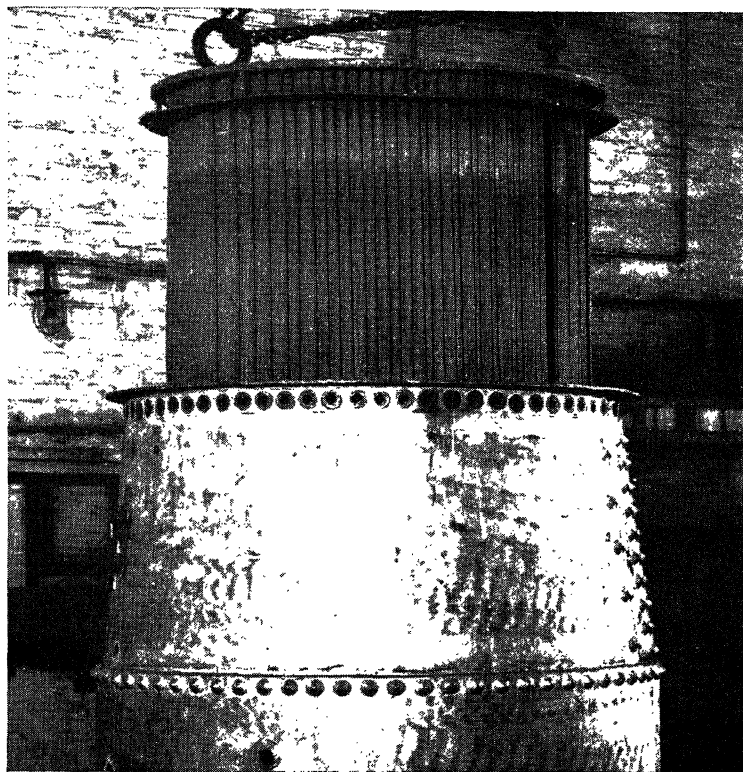


FIGURE 14. Boiler with copper tubes joined to headers with silver brazing alloy.

Heavy wall copper pipe was brazed into couplings and fittings with a silver brazing alloy. The assembly was then suspended from rods and loaded at the center so that the pipe was subjected to a uniform fiber stress of 5000 pounds per square inch. The pipe assemblies were then subjected to 100 applications of steam at 200-lb pressure and 425 °F, followed by the introduction of cold water into the pipes after each application of steam. Water was flowed until the temperature of the water



reached the temperature of the pipes; then steam was again admitted. This sudden change in temperature, combined with the load suspended from the mid-section of the pipes, subjected the joints to two severe shocks each cycle. The joints showed no failures and there was no evidence of flow at the temperature of 425 °F with a load considerably in excess of the creep limits of extra-heavy copper tubing.

A complete list of the industries that are adopting the silver brazing alloys to some extent for joining metals would include practically all of those that are fabricating equipment or articles from ferrous or non-ferrous metals which would not melt at temperatures below the melting points of these alloys.

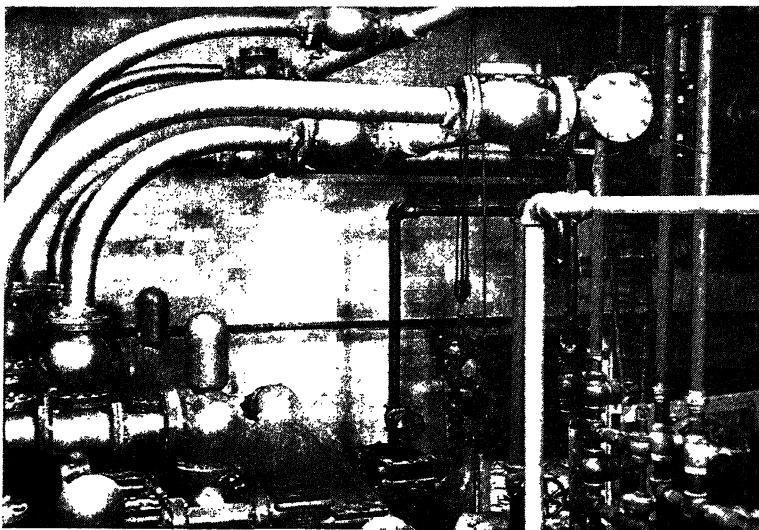


FIGURE 15. Silver-alloy-brazed flanges.

Silver brazing alloys cost more than base metal brazing alloys, because of their silver content, but this does not mean necessarily that joints made with them are more costly when all the factors which enter into making the joint are considered. First, as has been stated before, the strongest joints are made with very small joint clearances, and as a result a comparatively small amount of alloy is required. There have actually been cases where these alloys have replaced base metal alloys and the proportionate amount used was so small that there was an actual saving in the cost of the alloy itself. Even in those cases where the alloy cost may be higher there are economies, such as saving of labor and fuel, that may offset the difference in cost. Perhaps the most impor-

tant advantage is the reduction in rejections because of poor joints or damage which may occur from using the higher temperatures required for base metal brazing alloys. It can be definitely stated that there is no justification for the belief held by some persons that joints made with these alloys are expensive, and any engineer who is responsible for design of equipment should give them his earnest consideration.

### GROUP 3

The third group contains a series of alloys that approach the soft solders in their general characteristics but have somewhat higher melting points. Table 3 gives the composition of four of these alloys.

Table 3.—Special Silver Solders Melting Below 1000 °F.

No.	Silver (%)	Lead (%)	Copper (%)	Cadmium (%)	Melting Point (°F)	Flow Point (°F)
1	5-6	balance	—	—	579	715
2	2½	balance	—	—	579	579
3	2½	97½	½	—	580	661
4	5	—	—	95	640	740

It will be noted that their melting temperatures are somewhat above those of the common soft solders which melt at approximately 400 °F. They are used in those applications where the temperatures required for standard silver brazing alloys would be too high and at the same time the parts joined may be subjected to temperatures in service that would melt soft solders. Radiators for airplanes, and expansion valves on heating systems are examples. The strength does not compare with that of the joints made with other silver brazing alloys, but joints made with alloy No. 4 will have the same strength at 400 °F as soft solders at room temperature.

These alloys melt at such low temperatures that the workman has no color to guide him and in the case of Alloy No. 4 reports are often made that it is sluggish and will not flow freely. This alloy begins to melt at 640 °F but is not fluid until a temperature of 740 °F is reached; between these points it is sluggish, but if heated above 740 °F it will work satisfactorily.

Alloy No. 3 is a proprietary alloy which has been used successfully on railway and mine motors where the service conditions caused heating to a point where the standard lead-tin solders failed.

Another advantage claimed for the lead-silver over the lead-tin solders is that the latter tends to form a brittle copper-tin compound when used on copper. An article by Chadwick<sup>14</sup> discusses some tests that were made and confirms this statement.

### SILVER-CLAD METALS

As this chapter relates to hot-bonding with silver and silver alloys, some of the silver-clad base metals which are made by heat and pressure

are discussed in the following paragraphs. These composite metals are also called duplex and bi-metal.

Copper sheet or tubing is clad with fine silver or a silver alloy to obtain the benefits of a silver surface at a lower cost. The relative thickness of the silver and copper can be varied between wide limits, but the silver will seldom exceed twenty per cent of the total thickness and more often it will be ten per cent or less. Before the discovery of electroplating, all silver plating was done by bonding plates of silver and copper of the desired proportions and rolling the composite bar to the desired gauge. The famous Sheffield plate was made in this manner. An intermediate layer of a low-melting-point silver brazing alloy can be used, but it is not necessary in order to obtain a good bond between silver and copper. When a bar of silver is placed upon a bar of copper and the assembly heated above 1435 °F with the application of pressure, the silver-copper eutectic which melts at this temperature is formed, and a strong bond is produced. The pressure may be applied by passing through a rolling mill or by a suitable press. It is necessary to prevent the surface of the copper from oxidizing during the heating and pressing until the bond is made. The usual procedure is to clean the surfaces carefully and then, after assembling the bars, to brush a flux paste around the edges. Sometimes a light film of flux is brushed over the surfaces of the bars before assembling. The assembly is then heated in a suitable furnace and after being brought to the proper temperature it is rolled or pressed. If the bars are fastened together with sufficiently heavy clamps the bond can be made by heating the entire assembly.

When it is desired to have only part of the surface plated with silver, grooves of the proper width are cut in the copper bar and strips of silver are fitted into them. Heating and pressing are then performed and when the assembly is rolled down to the required gauge there will be alternate stripes of copper and silver. Striped stock for electrical contact points is made in this manner; the silver area is designed to be large enough for any particular service and the copper acts as a supporting arm. Silver-clad copper sheets and tubes are fabricated into tanks or other equipment where the corrosion resistance of silver is desired.

A similar procedure can be followed in making silver-clad phosphor bronze. Phosphor bronze has greater strength than copper, and when part of the bar is inlaid with silver and rolled down to thin gauges the arm will have the springy elastic character of the bronze. In bonding silver to bronze an intermediate layer of a low-melting-point silver brazing alloy will allow the bond to be made at a lower temperature.

Silver-clad steel has the strength of the steel and the corrosion resistance of the silver. Many chemical processes use both heat and pressure. In large-sized equipment the thickness of fine silver required to give the necessary strength would make the cost prohibitive. Although silver and iron do not form alloys in the generally accepted use of the term, it is possible to form strong bonds between silver and steel by applying

sufficient pressure at the proper temperature. Large sheets of silver-clad steel have been made in this manner. A heavy silver cladding would have about 20 per cent of the total thickness in silver, but other proportions of silver to steel can be made. Another method of making silver-clad steel is to use a silver brazing alloy for bonding the two metals together. A third method of cladding steel has been used, which involves the application of molten silver directly to the steel surface under properly controlled conditions of atmosphere and temperature.

Silver-clad nickel sheets are made in the same manner as silver-clad steel. They are more expensive but have the added advantage of the corrosion resistance of nickel.



## Chapter 8

# The Use of Silver in Bearings

By R. W. DAYTON \* AND C. L. FAUST \*

### INTRODUCTION

Bearings are used under widely different conditions of load, speed, and temperature. Since most bearings operate at moderate loads and speeds, they give no trouble in service, so that the generally known materials are adequate. In a few cases which concern high loads, the limitations of present bearings have been reached or even exceeded. Recent research on bearings has been directed toward development of high-strength bearings.

Bearings should operate under conditions of "fluid film lubrication" in order to give satisfactory service. For the present purpose, fluid film lubrication can be described as follows. A turning shaft carries a film of lubricant which separates the shaft and the bearing. Under proper conditions, the film is thick enough so that its properties can be calculated according to hydrodynamic theory. For this to be possible it must be at least several molecular diameters in thickness. The lubricant film prevents metal to metal contact so that the shaft is then actually "floating" in oil.

Fluid film lubrication is promoted by high rubbing speeds, low bearing pressures, high lubricant viscosity and good engineering. Such lubrication is characterized by low friction, a decreasing coefficient of friction with increasing load and decreasing speed or lubricant viscosity, and an absence of metallic wear. Fluid film lubrication is the desired state of bearing operation. Any other condition is dangerous.

Bearings run at high loads or too low speeds usually operate with "boundary film lubrication." In this case the oil film is so thin that hydrodynamic laws no longer apply. High friction and metallic wear result with boundary film lubrication. Some bearings are still designed to operate under such conditions, but the number is decreasing because of their unsatisfactory behavior. Rolling mill brasses are an old example of this type of bearing. On account of the unsatisfactory lubrication, there has been great activity in the development of better bearings for this service. Various types of brasses, fabric and roller bearings have been used in the attempt to obtain improvement. Proper design of the bearing, giving fluid film lubrication,<sup>1</sup> has been found to be one successful solution.

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The most difficult bearing service at present is operation at high, cyclic loads, high speed, high temperatures and in the presence of grit. In this class belong the big-end connecting rod bearings for aircraft, Diesel, truck, and automotive engines, named in the order of decreasing severity of service. These applications require fluid film lubrication for satisfactory performance, otherwise the large amount of frictional heat would cause almost instantaneous failure. Metals that have excellent bearing properties and proportionate fatigue strength at the temperature of service and some insensitivity to grit are necessary for these applications.

The mechanical properties of bearings are easily studied, whereas factors loosely called bearing qualities, are more difficult to define and measure. The distinguishing property of a bearing is the ability to permit a shaft to slide on its surface without frictional failure. Since all metals possess this attribute to a certain extent, the relative value for bearing use is indicated by the load carried without frictional failure compared with that supported by a standard bearing metal.

When a test bearing is operating with fluid film lubrication there is a slow decrease in the coefficient of friction as the load is increased at constant speed and temperature in a standard lubricant. At some load, the friction rises sharply, which indicates that boundary film lubrication has become operative. The load at which this friction rise occurs is called the "seizure pressure" because high friction causes actual seizing of the shaft in the bearing; especially in high-speed applications. The seizure pressure depends on the metal and design of the bearing, is truly a bearing property and is a very important factor. There appears to be little relationship between seizure pressure and the mechanical or physical properties of a material.

In the laboratory it is possible to test the seizure resistance of a bearing material in an Amsler machine. All the conditions of test must be carefully controlled.<sup>2</sup> The results have been found to indicate reliably the ability of a bearing metal to carry high loads in service.

Other properties of materials which should be mentioned because of their importance to bearing use are oiliness, embeddability and corrosion resistance. Oiliness is the ability of a metal to adsorb certain polar compounds of a lubricant.<sup>2</sup> When a bearing metal lacks this adsorptive power, grit in the oil or a rough finish on the shaft is likely to cause seizure at loads much lower than those necessary for seizure under optimum conditions. In the laboratory, oiliness is determined by tests against both polished and ground shafts, using a standard type of ground finish.

Embeddability is the ability of a metal to "soak up" grit, and seems to be a function of hardness. The softer materials have greater embeddability. A material which does not embed grit easily will score a soft shaft, and consequently must be run against harder shafts.

A bearing metal should be able to resist corrosion in oxidized oils. The present high engine temperatures tend to cause formation of corro-

sive compounds in oils, which then rapidly attack certain bearing metals. Since special treatment of the oils or of these materials is necessary to prevent such action, corrosion-resistant bearing metals are desirable.

The melting point of a bearing alloy is an important property. Bearings are used at elevated temperatures, often about 300 °F, and those materials which melt at low temperatures, such as babbitt, have only a fraction of their room-temperature strength at operating temperatures.

Only bearing metals suitable for heavy-duty service will be discussed here. Therefore, it may seem that the bearing properties of babbitt are being disparaged. This impression is to be avoided. Babbitt is a material which has an excellent balance of properties so that in the majority of bearing applications it is pre-eminent. It is not, however, the most suitable material for heavy-duty use.

### BEARING MATERIALS

Table 1 gives an outline of the extent to which the several available materials possess the properties required of bearing metals used in connecting-rod service. It is to be understood that all of these materials are used as linings of steel-backed bearings.

Table 1.—Properties of Bearing Alloys Commonly Used in Connecting-Rod Service.\*

Bearing Material	Seizure Resistance	Oiliness	Corrosion Resistance	Strength	Melting Point	Embeddability	Ease of Bonding
Babbitt	3	2	1	4	3	1	1
Cadmium base	3	3	3	3	2	2	2
Copper-lead	2	1	2	2	1	3	3
Pure silver	1	4	1	1	1	3	4
Silver-lead	1	2	1	1	1	3	5

### Babbitt

Babbitt bearings are very satisfactory for use at low loads. When loads are heavy and particularly when the loading is cyclic, babbitt is subject to mechanical failure. Only in automotive use is babbitt the most common connecting-rod bearing material. Even in this service, where the loads are about 1500 pounds per square inch, babbitt bearings fail by fatigue cracking. For heavier loads babbitt is being replaced by stronger alloys. A few years ago, there was a tendency in the automotive industry to replace babbitt by other materials. In service, corrosion and scoring were experienced with these other materials, so that in recent years there has been a change back to babbitt, care being taken to keep engine temperatures, and hence bearing temperatures, down to those suitable for babbitt.

### Cadmium Base Alloys

The two types of cadmium base bearings which are available have the same general properties. One type is a cadmium-nickel alloy<sup>3</sup> con-

\* Numbered in decreasing order of usefulness, 1 highest seizure resistance, 2 lower, and so on.



taining 0.7-3.0 per cent nickel, the other a cadmium-silver alloy <sup>4</sup> containing 2.25 per cent silver and .25 per cent copper. Since these alloys are stronger than babbitt they can be used at higher loads without fatigue cracking. They corrode badly in oxidized oil, and this fact has been largely responsible for their relatively small use. Indium plating of cadmium bearings has recently <sup>5</sup> been found to stop the corrosion. If economical, this method may be used to improve their status.

Cadmium bearings find use chiefly in automotive service and recently, to a minor extent in roll neck bearings.<sup>1</sup>

### **Copper-Lead Alloys**

Copper-lead is a generic term which includes a variety of alloys of copper containing large proportions of lead, usually with additions of hardening metals, such as tin, silver, nickel, or manganese. In the absence of such additions copper-lead alloys are very soft and weak. Common copper-lead types of bearings contain 25-30 per cent of lead with small additions of tin or silver. These alloys are the strongest of the common bearing metals and find large use in Diesel and aircraft service. For a time they were used to a small extent in automotive service, but scoring proved to be serious on the soft shafts then in use. Perhaps the advent of induction-hardened crankshafts will revive the use of copper-leads in automotive engines. Copper-leads are corroded by oil to a lesser degree than cadmium bearings. In spite of their high strength, fatigue failures of certain copper-leads occur in aircraft engines, where the bearing pressures may be 3000 pounds per square inch in normal service.

### **Pure Silver**

A recent development of the Allison Engineering Company was the pure silver bearing which had greater strength than copper-leads. These bearings had the requisite strength and were (usually) seizure-resistant in the heaviest-duty aircraft service. However, the results of a number of engine tests of silver bearings showed that silver was not entirely trustworthy because seizure would sometimes occur when the bearings were lightly loaded. Such seizures often occurred on bearings which had previously been more heavily loaded. Therefore, it was obvious that some property lacking in silver was necessary for trustworthy bearing operation. It was shown <sup>2</sup> in the laboratory that this missing property of silver was oiliness.

### **Silver-Lead**

Silver-lead alloys containing 3-5 per cent of lead have been found <sup>6</sup> to possess all the desirable properties of pure silver, plus oiliness. Although the technology of this material has not yet been completely worked out, it is likely that it will find use in aircraft and Diesel engines. There is little probability that silver-lead will be used in automotive

passenger car engines because the engineering requirements in such service are unlikely to be extremely severe. Truck and bus service may justify its use.

### Properties of Silver-Lead Alloys

Some properties of silver-lead alloys indicative of their value as bearing metals are given in Table 2. These alloys were made from high-purity metals, so that the amount of other elements present is negligible.

Lead has no apparent effect on seizure resistance against polished shafts, which is uniformly high, being about 10-30 per cent greater than that of a seizure-resistant copper-lead. As mentioned before, if the seizure resistance of a material is less against a ground shaft than against a polished shaft, the material is deficient in oiliness. Pure silver is seriously lacking in oiliness. In Table 2, the second column indicates that alloying the silver with small amounts of lead greatly improves the oiliness and about 3 per cent lead gives the required value. Against rougher shafts, more lead probably would be necessary.

The third column of Table 2 shows an interesting and unexplained fact in the results of seizure studies with corrosion-tested specimens. In all cases the corrosion testing greatly improved the seizure resistance, even that of pure silver. Apparently the long heating in the oil bath caused this improvement. This may have commercial significance and should be considered in further development of silver-lead bearings.

Since silver-lead alloys were not corroded by oxidized oil, there were

Table 2.—Some Properties of Silver-Lead Alloys

Lead Content (%)	Relative <sup>1</sup> Amsler Seizure Pressures—			Mechanical Properties—		
	Polished <sup>2</sup> Shaft <sup>3</sup> Chill Cast	Ground <sup>4</sup> Shaft Chill Cast	Corrosion Tested <sup>5</sup>	Brinell <sup>6</sup> Hardness	Shear Strength, (lb./sq. in.)	Hot Pounding <sup>7</sup> Resistance(%)
0.02	120	50	80	24	13,200	12.8
0.98	120	80	105	29	14,600	10.6
1.55	110	85	120	31	15,200	9.0
2.96	110	90	125	34	14,600	8.6
3.68	130	120	140	32	14,400	8.1
4.68	130	120	140	32	14,600	8.0

<sup>1</sup> The seizure pressures obtained in test are rated on the scale of 100 for 121 copper-lead. (28 per cent Pb, 1 per cent Ag, bal. Cu). Tests made at 250 °F, using SAE 30 Mobiloil.

<sup>2</sup> Polished with No. 4/0 emery, then buffed with rouge.

<sup>3</sup> Shafts are carburized SAE 2512 steel, hardened to 57 Rockwell C.

<sup>4</sup> Ground with No. 0 emery.

<sup>5</sup> The corrosion-tested specimens were heated for 8 days at 325 °F in an oil bath to which 1 per cent of oleic acid had been added.

<sup>6</sup> Brinell hardness with a  $\frac{1}{8}$ " steel ball, 100 kg. load applied for 30 seconds.

<sup>7</sup> Pounding deformation is the compression of the samples caused by striking a  $\frac{1}{2}$ " diameter,  $\frac{1}{2}$ " long specimen 100 blows with a 7.15-lb. hammer falling 2 in., tested at 300 °F.

no deleterious effects on seizure resistance which would be caused by corrosion.

The last three columns of Table 2 list some of the mechanical properties of silver-lead alloys. It is apparent that lead, in proportions up to 1½ per cent, has a slight hardening and strengthening effect. Additional proportions of lead up to 5 per cent have little further effect. This has been interpreted to mean that about 1½ to 2 per cent lead is soluble in solid silver. The strength increase is due to this solid solubility, so that increase in lead content beyond 1½ per cent would, according to this belief, have a slight softening effect.

The bearing properties and the mechanical properties of silver-lead alloys seem to be good enough for the most severe bearing service.

#### EFFECT OF IMPURITIES

Any method used for the manufacture of silver-lead bearings should be chosen with the aim of avoiding the presence of impurities, which almost uniformly have a very deleterious effect on seizure resistance.

Table 3 shows the large effect of small percentages of impurities. Silver electrodeposited from a bath of chemically pure materials had very high seizure resistance. An addition of 0.15 per cent of Cu-P cut this seizure pressure in half. Silver of 99.995 per cent purity, remelted under very clean conditions, had a markedly lower seizure resistance than electrodeposited silver.

Table 3.—Seizure Resistance of Copper-Lead Alloys and Various Types of Silver.

Material Tested	Relative Seizure Resistance
121 Cu-Pb (28% Pb, 1% Ag, bal. Cu)	100
224 Cu-Pb (25% Pb, 3% Sn, bal. Cu)	75
Electrodeposited and annealed Ag	165
Double-refined Ag, remelted	140
Ag bearing (contains some Cu)	115
Deoxidized Ag (with 0.15% Cu-P)	80

Ba, Bi, Li, Ca, P, and Sb are impurities which are extremely harmful to the seizure resistance of silver. Fortunately, none of these elements is found in commercial silver. Other impurities, such as Te, Hg, As, Al, Mg, Cu, Se, Cd, Mn, Zn, and Sn, are harmful in lesser degrees. Sulfur has a minor effect. Only one addition tested, Pb, had no apparent effect on seizure resistance.

#### INFLUENCE OF STRUCTURE OF SILVER-LEAD ALLOYS ON BONDING

For any bearing material to perform satisfactorily in heavy-duty engine service, it is necessary to bond it firmly to a backing which, in present practice, is usually steel. Because of their structure, silver-lead

FIGURE 1.

121 Cu-Pb bearing (27 per cent Pb, 1 per cent Ag, bal. Cu) on steel back (below). This alloy has excellent bearing properties, but because of the dendritic structure, it is relatively weak.  $\times 100$ .



FIGURE 2.

224 Cu-Pb (25 per cent Pb, 3 per cent Sn, bal. Cu) on steel back (below). This alloy has good strength because the dendritic structure of the lead is broken up by the tin addition. The frictional properties are not as good as is desired for aircraft use.  $\times 100$ .

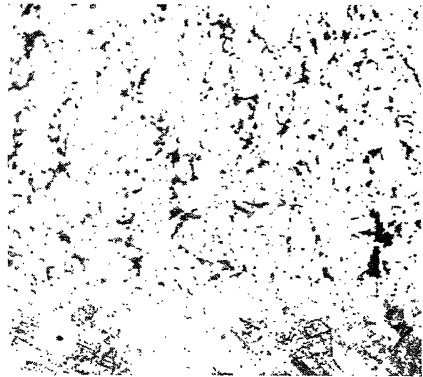


FIGURE 3.

Silver (with small additions of Cu only) on steel back (below). This material is amply strong and seizure-resistant for aircraft use, but because of its lack of oiliness, it must be run against smooth shafts and in the absence of grit.<sup>s</sup>  $\times 100$ .



alloys are difficult to bond to steel. It is therefore advisable to discuss structure at this point.

The structure is indicated by the constitution diagram of silver and lead, which is reported<sup>7</sup> to be a simple eutectic diagram with limited solid solubility. The eutectic point is placed at 2.5 per cent Pb and 304 °C (579 °F), which is 23 °C (41 °F) under the melting point of lead. There is very little solid solubility of silver in lead, but an appreciable solid solubility of lead in silver. A study indicates a solubility of between 3.68 and 4.68 per cent Pb in silver at 570 °F (299 °C), and 1½ per cent Pb at 300 °F (149 °C).<sup>6</sup>

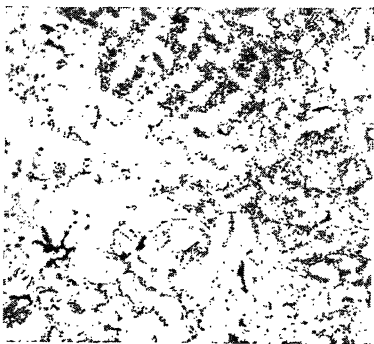


FIGURE 4.  $\times 100$ .

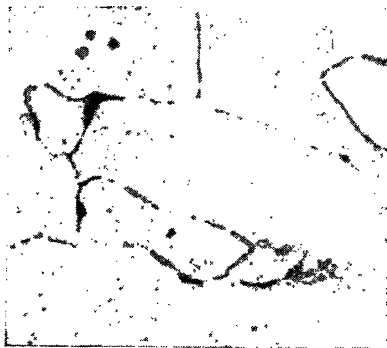


FIGURE 5.  $\times 1000$ .

Sand-cast alloy of silver containing about 4 per cent of lead. The low magnification shows that some lead is present as dendritic traces in the silver grains; high magnification shows that there is a considerable amount of lead along grain boundaries, giving rise to intergranular weakness to which cast alloys of Ag-Pb are prone.

Silver-lead alloys, therefore, usually consist of two phases, a silver-rich solid solution and nearly pure lead. In freezing, lead segregates at grain boundaries, if the lead content is sufficiently high, as shown by Figures 4 and 5. The presence of lead along grain boundaries causes weakness, particularly at high temperatures. Figures 6 to 9 show that this segregation occurred in a 4.68 per cent Pb alloy, causing it to crack along grain boundaries when heated for a long time at a temperature close to the melting point of the eutectic. Since a 3.68 per cent Pb alloy did not crack during the same heat treatment, the maximum lead content at which intergranular cracking can be avoided is apparently between 3.68 and 4.68 per cent Pb.

Diffusion experiments at high temperatures revealed the same tendency. When heated at temperatures above the melting point of the eutectic, lead penetrates into silver along grain boundaries, as shown in Figures 10 and 11. When a lead-plated (0.00015-in. Pb coating) silver bearing was heated, the lead penetrated along grain boundaries to the

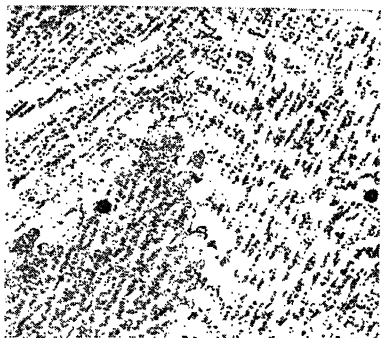


FIGURE 6. Chill cast.

FIGURE 7. Annealed at 570 °F  
for 2 days.

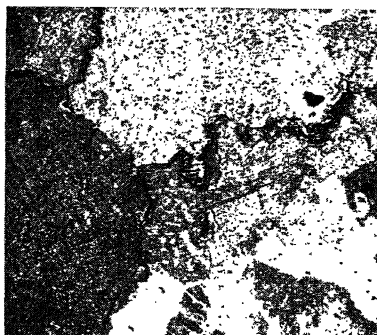
In this alloy, which contains 3.68 per cent Pb, all of the lead is present as interdendritic material, none along grain boundaries, so that the high temperature anneal has had no effect on structure.  $\times 100$ .

steel back and weakened the silver-to-steel bond so that the silver lifted away from the steel.

The intergranular weakness due to lead segregation appears to be characteristic of the thermally prepared Pb-Ag alloys. Such segregation is directly responsible for poor bonding of the alloy when cast on steel backs, because of accumulation of lead at the alloy-to-steel interface. Electrodeposition (or what amounts to "cold" casting) should produce the Pb-Ag alloy with no thermal segregation. It is apparent from Figures 12 and 13 that the as-plated alloy shows no evidence of crystal



FIGURE 8. Chill cast.

FIGURE 9. Annealed at 570 °F  
for 2 days.

In this alloy, which contains 4.68 per cent Pb, there is some lead present along grain boundaries as well as within the grains. Annealing this alloy causes many intergranular cracks to open up, because of the low strength of the intergranular material at the temperature of the anneal.  $\times 100$ .

boundaries or lead separation. Annealing caused a recrystallization (Figure 13) but no lead separation in the electrodeposited alloy. As long as the temperature of the anneal was less than 577 °F (the melting point of the eutectic) annealing times of one to eight hours caused no evidence of lead separation at the grain boundaries or at the interface between steel back and the alloy plate (Figures 13 and 14).

It therefore appears that electrodeposition provides a satisfactory method for producing Pb-Ag bearing liner on steel backs. The production man and the engineer will naturally desire to look into the advantages as well as the disadvantages of the electrodeposition method.

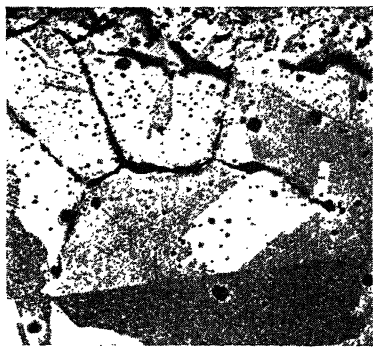


FIGURE 10. Diffusion of 0.001" of Pb into pure Ag at 1540 °F.  $\times 100$ .

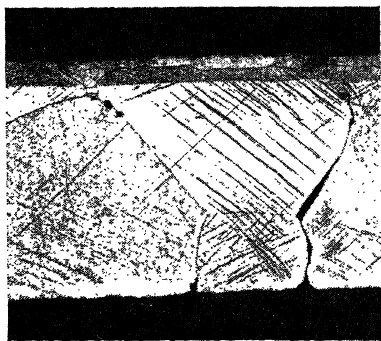


FIGURE 11. Diffusion of 0.00015" of Pb into Section of Ag bearing at 1500 °F.  $\times 100$ .

These photomicrographs show that at high temperatures lead will penetrate along the grain boundaries of silver, giving rise to intergranular weakness. In the case of the silver bearing, the lead has penetrated to the silver-steel bond (bottom of picture) and the silver layer has lifted from the steel. This effect is undoubtedly the reason for the lack of bonding in thermal methods of lining bearing shells with silver-lead.

Certain advantages are fairly evident: (1) The steel backing can be of any desired hardness without danger of heat tempering, since the plating and annealing temperatures are relatively low; (2) there will be little scrap loss since the electrodeposited lining requires a minimum of machining; (3) usually the alloy can be deposited just as readily on the inside as on the outside of the back of the bearing; and (4) since the alloy is deposited with a uniform structure of very fine grain size, subsequent annealing can produce softer plates for better seizure resistance, if required, and still maintain a uniform small grain size.

To one not closely acquainted with electrodeposition of alloys, this method of manufacture might be considered a disadvantage. One acquainted with alloy deposition would not be inclined to such a conclusion, but would only demand that: (1) the as-plated metal should have a uniform composition and hardness or, if too hard as-plated, be

FIGURE 12.

Electrodeposited alloy (sample D-8) of 3.3 per cent Pb, bal. Ag, as plated. The hardness is 92-112 Vickers Pyramid. The plate is ductile. There are no traces of crystal boundaries, lead is randomly distributed.  $\times 1000$ .



FIGURE 13.

Same sample as Figure 12, after annealing for 1 hour at 550 °F. The hardness has been reduced to 45 Vickers Pyramid, and the plate is very ductile and tough. Recrystallization has occurred, apparently leaving voids in the structure. Lead is still randomly distributed.  $\times 1000$ .

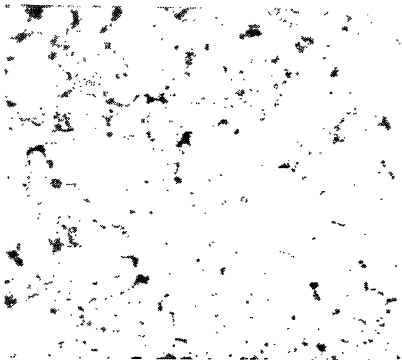
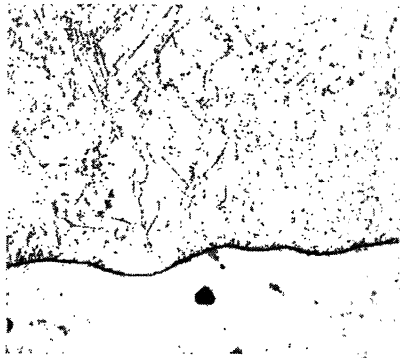


FIGURE 14.

Ag-Pb alloy deposited on steel back (below) and annealed for 8 hours at 550 °F. The plate is still adherent to the back, indicating that grain boundary weakness will not destroy the bond of plated bearings, unless the annealing is done at a higher temperature than the melting point of the eutectic. (577 °F.)  $\times 500$ .





subject to suitable annealing; and (2) the alloy should be plated in a process that gives suitable reproduction of results with reasonable control of the several variables involved.

Both of these requirements have been met by laboratory study of the electrodeposition process. A feasible method has been discussed<sup>9</sup> for depositing Pb-Ag alloys containing 3 to 4 per cent Pb. The advantages of the process have already been pointed out. The subsequent discussion considers one electrodeposition process that has been found to give the desired bearing alloy. It has been demonstrated that certain operating conditions can be expected to give reproducible results from the following plating bath:

	<i>g./l.</i>	<i>oz./gal.</i>
Potassium cyanide	22	3
Silver cyanide	30	4
Potassium tartrate	47	6.3
Potassium hydroxide	0.5	0.067
Basic lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$ )	4	0.53

When preparing this bath, the silver cyanide should be dissolved in a solution containing the potassium cyanide. The lead salt should be dissolved in a solution containing the potassium tartrate and potassium hydroxide. The clear solutions are then mixed together to form the plating bath.

Good results are obtained at a bath temperature of 74 to 90 °F. At 5 to 15 amp./ft.<sup>2</sup> comparatively smooth, dense and fairly ductile plates contain 3.3 to 3.5 per cent Pb. The plates were made up to 0.030 inch in thickness, with the indication that much greater thicknesses could be produced. The hardness, as plated was about 126 Vickers\* and could be lowered to around 45 to 60 by annealing for 1 hour at 550 °F.

Alloy anodes, containing 3.8 per cent Pb-96.2 per cent Ag dissolve suitably at 5 to 10 amp./ft.<sup>2</sup>, to maintain the necessary Pb/Ag concentration ratio in the bath. Anodes cast in a warm, graphite mold have a suitable grain size and uniformity.

A good example of the uniformity of plate composition is shown by the results on test bearings. On the flange, where stirring and current density might be expected to be somewhat greater than on the face of the bearing, the plate contained 3.3 to 3.5 per cent Pb. After plating, this flange plate and about 0.010-inch from the bearing surface were removed by machining. Analysis of the turnings from the last fine cut to give the right liner thickness showed 3.3 to 3.5 per cent Pb.

The anode current efficiency is slightly greater than that of the cathode. This fact is advantageous in commercial plating, because the excess metal addition can serve to offset drag-out losses. Thus the need for making additions of metal salts to the bath is eliminated or, at least, minimized. The best results are obtained with agitation of the bath

\* Diamond point indentor with 1 kg. load.

during plating. An increase in current density on both the anode and the cathode, should be accompanied by a suitable increase in agitation. The anode and cathode efficiencies, under conditions that are described, are nearly 100 per cent.

The hardness, ductility, uniformity of plate composition and thickness of the alloy deposit, and the optimum anode dissolution depend on several factors, *i.e.*, current density; temperature; uniformity of bath agitation; Pb/Ag ratio, pH, concentration of cyanide, tartrate and carbonate in the bath; and metallic impurities in the anodes, hence ultimately in the bath. The suitability of any alloy plating bath to produce a given alloy plate is governed by these variables. The economics of the process depends on the limits within which the above factors can vary, without causing any practical effect on the properties and composition of the alloy deposited.

In the bath that has been described, the current density, temperature and agitation can vary within reasonably wide limits without any significant change in composition or physical properties of the plate. This is an important fact, since relatively complicated shapes can receive an alloy plate that is within the required limits of uniformity. The control that has been required was no more exacting than any plating department can maintain with reasonable care. The bath can be analyzed by standard methods and when suitably maintained should receive the proper Pb/Ag replacement from the anodes.

Potassium salts in the experimental baths permitted softer and more ductile plates than analogous baths made up with sodium salts.

A current density and temperature range have been given. The limits of agitation are difficult to define, because of dependence on tank size, shape and methods of racking. However, this can be established for each installation. Too rapid stirring causes an increase in hardness of the alloy deposited. The same effect is caused by too large an increase in hydroxide and free cyanide concentration. An increase in current density tends to increase the percentage of lead in the plate. An increase in temperature in general tends to decrease the percentage of lead in the plate, to decrease the plate hardness and increase its ductility. Apparently some variation in cyanide, hydroxide and tartrate composition can be tolerated with relatively little effect on the plate composition. The cyanide, tartrate, and hydroxide are essential to the obtaining of uniform and complete anode dissolution. Anyone using this bath should provide the anode current density, which, at the given condition of bath agitation, causes the anodes to show a crystalline or very bright, smooth appearance. Too high current density or too slow bath agitation causes the anodes to film and drop off slowly soluble sludge. The sludge causes rough plates. Too low anode current density causes irregular anode dissolution. At anode and cathode current densities over 3 and 5 amp./ft.<sup>2</sup> respectively, some bath agitation is necessary to secure sound,

dense plates and suitable anode dissolution. Too high cathode current density or too little agitation causes spongy, non-adherent plates.

The plating time to obtain a given thickness of alloy deposit depends on the current density. At 5 amp./ft.<sup>2</sup>, about 0.001 in./hr. of plate is produced; at 15 amp./ft.<sup>2</sup>, about 0.003 in./hr.

A complete survey of plating conditions has not been made. The process just described is the only one which has been shown to be apparently capable of long-time use in production. Anyone desiring to electrodeposit such a Pb-Ag alloy for bearings should use these data to help in establishing an active knowledge of the variables involved. Further study should be made on a small-scale pilot plant basis, in order to study control factors over a period of a significant amount of plating.

Other studies, of a preliminary nature, on codeposition of Pb and Ag are described by Mathers and Johnson.<sup>10</sup>

#### TESTS ON FULL-SIZE, ELECTROPLATED SILVER-LEAD BEARINGS

Two full-size silver master rod bearings were bored oversize and then electroplated with an alloy of about 3.5 per cent Pb, balance Ag. After the plating they were annealed for 5 hours at 500 °F, followed by 4 days at 350 °F. The bearings were then bored to the correct size and tested<sup>10</sup> in a bearing testing machine of the Pratt & Whitney Aircraft Company. This machine is similar in principle to the General Motors type of bearing tester, except that only one bearing is used, so that the load is carried by all parts of the test bearing, as it is in a radial engine.

Table 4.—The Seizure Resistance of Various Bearings as Determined in the Pratt & Whitney Engine Type of Bearing Tester.

Designation of Bearing Material	Approximate Composition	Speed to Obtain Seizure (R.P.M.)	Bearing Pressure at Seizure (lb. per sq. in.)	Remarks
Silver Bearing	99.5% Ag, balance Cu	2650	3410	
224 Bronze	25% Pb, 3% Sn, balance Cu	3000-3200	4380-4980	This type of bronze resists fatigue cracking in aircraft service.
Plated Bearing, C-3	3.02% Pb, balance Ag	3400	5620	Electroplate 0.006" thick on silver bearing.
Plated Bearing, C-4	3.31% Pb, balance Ag	3700	6650	Electroplate 0.0025" thick on silver bearing.
121 Bronze	28% Pb, 1% Ag, balance Cu	over 3950	over 7590	This material is not sufficiently fatigue-resistant for continuous service at this load.

NOTE.—These tests are made against a finely ground shaft of carburized SAE 2512 steel hardened to 57 Rockwell C. Because the shaft is ground and not polished, a pure silver bearing does not have an extremely high seizure resistance.

The results (Table 4) showed definitely that the silver-lead bearings were more seizure-resistant than those of pure silver or than 224 Cu-Pb, although they did seize at lower speeds and loads than 121 Cu-Pb bearings. The failures which occurred seemed to have originated as bond failures, rather than as frictional ones, so that the seizure test results which have shown silver-lead bearings to be more seizure-resistant than

121 Cu-Pb are not disproved. The conclusion previously stated, that a silver-lead alloy is the most seizure-resistant material known, is still strongly supported.

The results on these two test bearings were very encouraging, and tend to support the findings that silver-lead bearings should be a most suitable material for extremely heavy-duty service, once a good manufacturing technique for bonding them to a steel back has been established.

Although the foregoing results indicate a bonding problem when the Pb-Ag bearing alloy is electrodeposited, it is considered that a suitable preparation and strike plating procedure is known. Preliminary tests have given good results on steel, by using brass and silver strike plates before the alloy plating.

There is experimental evidence that electrodeposited metals give better bearing performance than their cast, thermal counterparts. This fact would be another advantage favoring the electrodeposition method of making Pb-Ag alloy bearings, or pure silver bearings, or for that matter, any bearing.



# Chapter 9

## Coatings

By LAWRENCE ADDICKS AND A. J. DORNBLATT

### THE PROBLEM

It is obvious that the extent to which commercial applications can be developed for utilizing the desirable surface properties of a relatively expensive metal, such as silver, will depend upon how much surface area per unit of weight can be supplied. In other words, what are the practical limitations of silver as a coating upon a cheaper backing material which will give the necessary strength? There are many methods of producing such a coating and they fall rather naturally into a classification by thicknesses, varying from the very thin ornamental and optical applications, where perfect continuity of surface is not essential, to massive construction where the backing metal is unnecessary and the "coating" becomes a solid silver article. It is also possible to make very complicated one-piece structures of pure silver by electroforming as described in Chapter 10, and these in turn may be given a base metal backing by electro-deposition if desired.

Specifically, we are concerned with determining the thickness of silver coating required which will simultaneously protect the backing of a vessel against corrosion, secure its contents against contamination, give adequate life (corrosion plus erosion) and compete successfully in price with rival materials, such as tin, nickel, aluminum, stainless steel, special iron alloys, lacquers, glass, ceramic wares and rubber. Many additional factors enter into making a choice of material to be used for a specific purpose, such as taste, odor, frangibility, weight and thermal conductivity. Where external heat is to be applied, high thermal conductivity provides not only the direct advantage of greater daily output but the indirect one of limiting the time available for undesirable by-reactions in chemical work. The Project undertook to examine every conceivable method of producing coatings and to determine in each case (a) adherence, (b) relation between thickness and porosity, (c) relative cost of method and (d) time required—an important question in mechanical mass production. For silver to be used in any given application it must be shown either that the advantages gained compensate for the added cost or that no greater cost is entailed because less metal is required due to the suitability of a thinner coating or because of a higher scrap return.

## THE METHODS

The available methods of making a silver coating may be listed as:

- (a) Welding (fine silver sheet)
- (b) Spraying
- (c) Cladding (rolling duplex ingot)
- (d) Hot dipping
- (e) Electroplating
- (f) Chemical reduction
- (g) Vaporization
- (h) Cathode sputtering

Speaking very generally, the order stated is from thick to thin, but no one method can command the whole range of applications; (a), (b) and (c) have no upper limits of thickness but very decided lower ones; (d) and (e) cover an intermediate range; (f), (g) and (h) find application in very thin coatings.

At the outset we can set aside welding, spraying, hot dipping and cathode sputtering as of very limited application to special cases. The welding of thin sheets of silver to a metallic back is feasible but difficult, owing to the high thermal and electrical conductivity of silver. Spraying is a useful method in inaccessible places but, owing to the gross structure of the coating produced, it requires a heavy deposit to overcome inherent porosity, and adherence is not all that might be desired. Molten silver does not "wet" iron, so that hot dipping is not practicable on such a backing—at least in air and without special procedure—and hot-dipped coatings are notoriously porous. Cathode sputtering is slow and cannot compete with vaporization in commercial application.

We therefore have to deal with breaking down thick coatings, as in the production of clad metals, or building up thin ones as in the case of the other methods. When rolling down duplex ingots it is evident that at some thickness the coating will show bald spots, which destroy its usefulness. While experience has shown that this critical thickness may be well below 0.001 inch, it is evident that cladding normally belongs in the larger field of tanks, vessels, etc., as it is less expensive to build up a very thin coat than to roll down a thick one too far.

The mechanism of building up a deposit is probably the same, whether it is produced electrolytically, chemically or by vaporization. A scattering of tiny nuclei is presumably formed on the base material, and growth spreads out from these centers until the edges touch, giving opacity with a coating of varying thickness and pores near crystal complexes or around any foreign body. At what average thickness porosity is overcome it is hard to say, but under ideal conditions it is probably not far below 0.00001 inch, regardless of the method.

In the case of coatings 0.0001 inch thick or less, three methods may be considered to have commercial possibilities. These are electroplating,

chemical reduction, and vaporization. Electroplating is discussed in detail in Chapter 10, and chemical reduction and vaporization in Chapter 11. The two latter methods are of interest for coatings from 5 to 100 millionths inch thick. The chemical and vaporized coatings are probably feasible only if deposited upon a suitable organic material, and the electroplated coatings only if deposited upon a metallic surface, or upon an organic surface made conducting by the deposition of a metallic film applied by chemical reduction, vaporization, or as a metallic-pigmented lacquer.

#### FIELD OF APPLICATION

The suitability of a silver-lined or coated object is dependent to a very great extent on the application for which it is intended. The field of application is determined by, and in turn tends to determine, the thickness of the silver coating. An arbitrary division in application can be made in terms of the thickness of the silver coating. Coatings 0.001 inch or more in thickness would find application in returnable shipping containers, which require coatings of substantial thickness because of the service conditions. The initial cost of a returnable container is a less important factor than is that of one to be discarded, and considerations of quality, convenience, and sales appeal may well justify the silver lining. Coatings less than, say, 0.0001 inch thick involve silver costs less than 3 cents per square foot, and make it possible to consider silver for lining low-cost non-returnable containers, which, because of less severe requirements, can utilize thinner coatings.

As examples of non-returnable containers may be mentioned cans for beverages and foodstuffs. Containers for certain pharmaceuticals, cosmetics, and chemicals might also be included in this class, but the service requirements for these applications may necessitate somewhat thicker coatings than others in this category. The cost of the container is relatively small compared to the sales value of the contents, and ruggedness and ability to withstand abuse is of secondary importance. Examples of returnable containers are drums, barrels, cans, pails, and the like. These must be rugged, long-lived and refillable.

#### COST

The price of silver is currently quoted in cents per troy ounce, whereas the engineer is accustomed to making calculations based on the cost per avoirdupois pound. To convert the price of silver in cents per troy ounce to dollars per avoirdupois pound, it is necessary to multiply by 0.14583 (or, in round numbers, the price of silver in cents per avoirdupois pound is 15 times the price per troy ounce). To calculate the cost of a silver coating, the weight per square foot for a given thickness is also needed. Since a sheet of silver, one square foot in area and one mil (0.001 inch) thick, weighs almost exactly 0.8 of a troy ounce, its value in cents is eight-tenths of the current market price for silver, expressed in cen-



troy ounce. If silver is quoted at 35 cents per troy ounce (\$5.10 per avdp. lb.), for example, a coating 1 mil thick has a silver value of 28 cents, per square foot, a coating 100 millionths inch thick a value of 2.8 cents, 10 millionths inch thick a value of 0.28 cent, and a millionth inch thick film about .03 cent per square foot of area.

### DESIGN OF SILVER-LINED CONTAINERS

The design of silver-lined containers requires an approach to the problem free from any tendency to take a conventional design and merely try to coat it with silver. However, it is not believed that problems will arise which cannot be successfully solved by the application of simple and established principles.

### Silver Coating by Chemical Reduction or Vaporization Methods

It is to be recognized immediately, in considering silver coatings of the order of a few millionths of an inch in thickness, that it is unlikely that a pore-free coating can be produced commercially. This limits such coatings to applications where no possibility of galvanic corrosion exists, or where, if it exists, no serious damage can result. For many ornamental or decorative applications, particularly as applied to molded plastics, a silver film about 5 millionths of an inch thick is practically opaque and the pin-holes which might be present would not be detected by the unaided eye. Exposure of the very limited area of plastic uncovered at minute pores will normally be of no consequence. For silvering transparent plastics, consideration must be given to the difference between the vaporized and chemically reduced films when looking at the side of the metallized surface away from the plastic (front reflection), as the chemically reduced film is generally less bright than that produced by vaporization. The chemically reduced film has one surface that tends to be somewhat of a frosty or matte appearance. When viewed through the plastic (back reflection), the silver films produced by either method are of brilliant quality; but in the case of certain plastic materials, the silvering solutions stain the plastic and an unsatisfactory back-reflecting surface is obtained. Adherence is a variable which seems to depend on the chemical character of the organic material; but even in the case of deposits with initially poor adherence, it often was improved on aging the silvered material at room temperature, or at somewhat elevated temperature for a shorter time. In production, it may be possible to overcome adhesion difficulties by applying a suitable transparent lacquer. In compacts and other objects made of transparent or translucent material, including glass bottles, metallizing with silver gives a beautiful effect. Often it is possible to protect or cover the front surface of the silvered area by a lacquer, fabric, or equivalent, without detracting from the brilliance of the silver as seen through the plastic. The most satisfactory coatings for silvering appear to be those which are glossy in finish and relatively heat-resistant.

It appears commercially feasible to silver cans by the chemical reduction or vaporization method, provided the metallic shell is first coated with a suitable organic film. This organic coating must give complete protection to the steel. It should be selected on the basis of cost, adhesiveness, flexibility, protection afforded the steel, and suitability as a basis upon which the silver can be satisfactorily deposited. The silver lining will give the can a remarkably attractive appearance, and will reduce, if not entirely prevent, any effect of the organic coating on the flavor of its contents. Cans made in this manner need no tin coating, and the organic coating can be selected without reference to the effect of baking temperatures upon the tin coating or solder. A seamless can is to be preferred for such a container, but if a soldered side seam is used, a high-melting lead-silver solder can be used to permit high baking temperatures. It is essential that the can body and ends be coated before assembly to avoid crevice corrosion, and insure complete removal of volatile constituents from the organic coating.

### Silver Coating by Electrodeposition

Silver-plated one-trip containers call for a very thin silver coating which would also have to be pore-free. In Chapter 10 it is shown that a copper coating, about 1 mil thick, can be deposited in pore-free condition upon commercial steel of good surface quality. Upon such an undercoat, very thin, pore-free silver deposits can be produced. A promising possibility in this direction is the plating of seamless cylindrical can bodies, and flat sheet from which the ends may be blanked. In general, forming after plating would be limited to a lock-seam or beading operation.

Where heavier silver coatings are permissible, the can may be assembled from parts made by pressing or drawing operations as also outlined in Chapter 10, using a rolled lock-seam. Care must be taken to avoid exposure of any raw edges, and the pouring spout must have the edge turned outward rather than inward as is customary.

Similarly, drums can be silver-lined by plating the cylindrical body shell before the ends are attached, and plating the drum ends before assembly. The plated material will withstand the necessary lock-seaming operation. The cylindrical drum body must be protected on the outside from contact with the silver bath, but this can be done by the use of a suitable stop-off or a molded non-conducting jig which clamps around it and prevents free access of the electrolyte to the outside. It should be mentioned that the side-seam of the drum must be very smooth. This can be accomplished by butt-welding, followed by surface grinding, or preferably by silver brazing.

The simplest design for a silver-lined shipping container is probably the 3-piece drum, consisting of bottom, shell, and top. If the container is to be refillable, the top should be completely detachable, provided with an outside clamping and locking device. If fittings must be used, they should preferably be located in the head, and consideration should be

given to the use of fittings held in place by a gasket and an outside locking nut. As the fittings must generally be silver-plated also, they should be designed for this purpose. Castings are difficult to plate satisfactorily and fittings assembled by brazing from wrought tubing and sheet, or else forgings, are preferred. Stainless steel might be employed, also possibly bronze or brass, but the possibility of corrosion by dissimilar metals in contact, or contamination by the less noble metal, must be considered.

The limitations of silver-plated material for applications requiring brazing are discussed in Chapter 10 and need not be anticipated here. If it is not possible to design the container so as to avoid the necessity for joining by a method involving heating, then silver brazing using induction heating should be considered in laying out the design. The possibility of using a corrosion-resistant tin-silver alloy as a solder should not be overlooked.

The steel selected for such applications as those under discussion must be purchased with an eye to the requirements which it must meet. Material to be plated should be of a superior surface finish and quality. In general, the thinner the coating to be applied, and the less the cost of preparation for plating, the better the surface finish must be. For this reason cold-roll finished steel is preferable to hot-roll finished material. Where forming operations are involved, a sufficiently ductile steel is required. It may be advisable to purchase steel of the quality used in fabricating electroplated commodities such as electric appliances, even though the cost is higher than run-of-the-mill steel, for this may be an economy in the long run. Deep scratches, slag inclusions, blisters, etc. favor the formation of pores or defects in plating. An experienced operator can judge the surface quality of the steel by visual inspection. The cost of special quality steel in small lots may warrant consideration of the use of brass rather than steel as the base metal. Brass offers the advantage of freedom from edge-corrosion and may be more desirable for objects like ointment boxes and decorative items.

The technique of plating is discussed in Chapter 10, where it is pointed out that conventional practice can be followed, provided scrupulous care is taken to keep the plating solutions free from suspended matter.

# Chapter 10

## Electroplated Silver Coatings

BY A. J. DORNBLATT \* AND A. C. SIMON †

### I. INTRODUCTION

In view of the potential market of very substantial proportions for containers such as barrels, drums, and cans possessing the corrosion resistance of silver, provided such containers are not too costly, research was undertaken at the National Bureau of Standards on silver plating as a method for economically producing silver-coated sheet. The use of steel-backed silver bearings in the aviation industry, coupled with the discovery by Dr. R. W. Dayton (see Chapter 8) that electrolytically pure silver has superior bearing qualities, prompted a simultaneous study of methods for depositing thick silver coatings on steel under the sponsorship of the Silver Project at Indiana University. Experimental work reported in Section II of this chapter deals with the development of satisfactory methods for the production of thick silver plate (0.01 inch minimum) on steel, suitable for bearings and service in the chemical industry; and research on methods for depositing relatively thin silver coatings suitable for use in the fabrication of (a) silver-lined returnable shipping containers, such as barrels and drums, with a coating of moderate thickness (0.001 inch minimum) and (b) silver-lined non-returnable containers, such as cans, with a coating of minimum thickness (0.0001 inch maximum). Section III of this chapter reviews the work on the electro-deposition of silver alloys, also sponsored by the Silver Project, at Indiana University.

### II. RESEARCH ON SILVER PLATING FOR INDUSTRIAL PURPOSES

#### 1. Scope of Research

Satisfactory silver-lined containers and bearing shells require (a) pore-free deposits of an acceptable thickness, (b) adhesion of the coating to the base metal, adequate to withstand fabrication of containers from the plated sheet by commercial methods, and (c) low-cost plating methods.

The problems studied were those connected with the development of procedures by which these requirements could be met.

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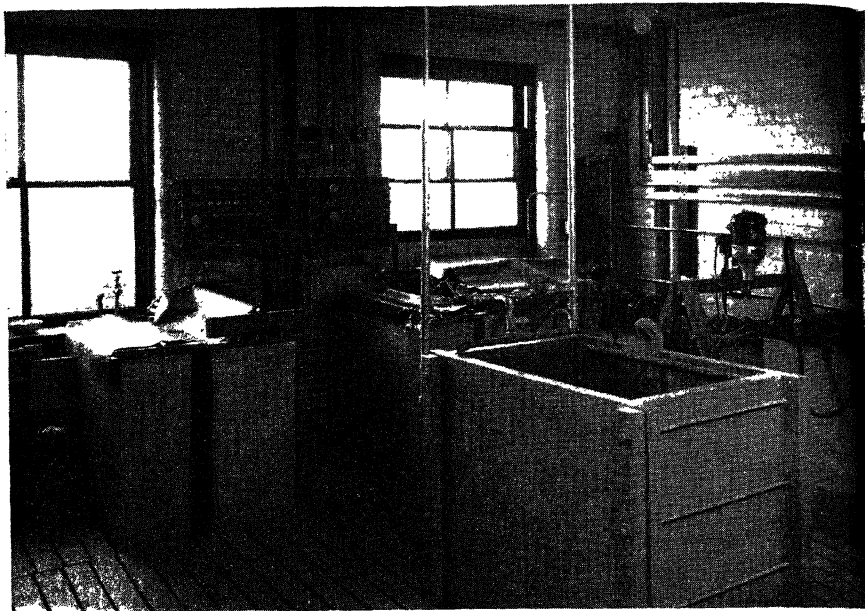


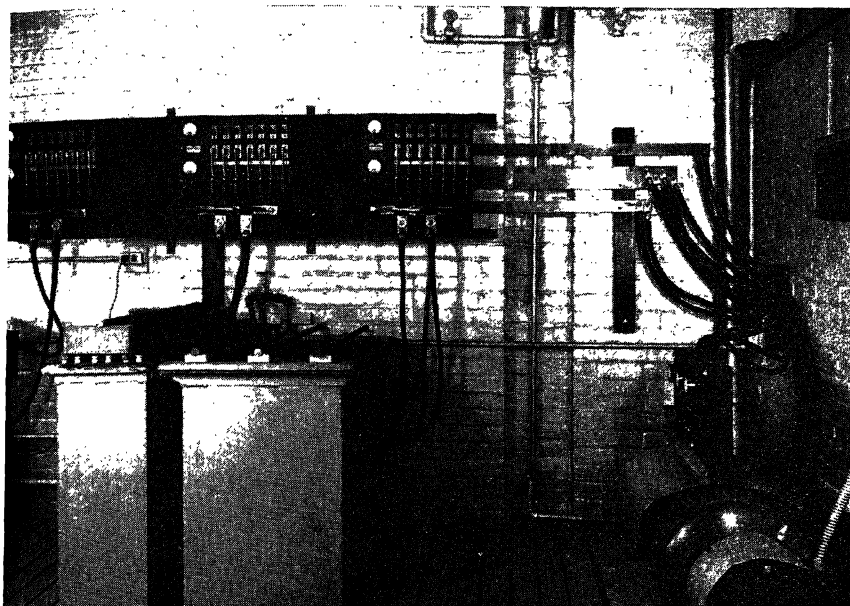
FIGURE 1. View of pilot plating plant

## 2. Materials and Test Methods Used

### (a) Base Metals Used

The characteristics of the metals used in the plating studies at the National Bureau of Standards are given in Table 1. The steel of lot number 1 is a grade used in the manufacture of pressed steel barrels. Circles of this material 23 inches (584 mm) or 30 inches (762 mm) in diameter were plated, back-to-back, on moving cathode racks in rubber-lined tanks such as are shown in Figure 1, 3 feet long, 3 feet deep, and 20 inches wide, containing approximately 100 gallons of electrolyte. Sheets of lot number 5, 26×26 inches (660×660 mm), were plated in the same manner.

The steel of lot number 4 is representative of material used for seamless can bodies. Steel of lot number 5 is a commercial grade of high-quality, deep-drawing stock available in a bright finish that was used in studies of porosity, adhesion, forming and embrittlement. Lot number 8 is a commercial grade of copper, selected because of its physical and chemical homogeneity, for studies on adhesion and porosity. Lot numbers 2 and 6 are material not used in any of the experiments discussed.



at National Bureau of Standards.

Table 1.—Metals Used in Plating Studies.

Lot	C	Mn	—Composition (%)			Cu	Description	Thickness (in.)
			P	Si	P			
1	.05	.37	.007	.013	.01*		Flange quality deep-drawing steel. Hot-rolled, pickled finish.	0.050
	.09	.32	.007	.031	.01*		Low - carbon steel. Cold - rolled, satin finish.	0.030
	.07	.41	.010	.027	.01*		Commercial can stock of deep - drawing quality. Mill finish black sheet.	0.012
	.05	.30	.015	.026	.01*		Low-metalloid, rimmed open - hearth steel. Cold - rolled bright finish. Automobile body stock.	0.009
	.10*						Low-carbon steel, cold-rolled by polished tungsten carbide rolls. Mirror finish.	0.009
						99.98	Oxygen-free, high-conductivity copper. Polished to a mirror finish.	0.012

\*Less than.

Table 2.—Typical Solutions and Operating Conditions Used.

No.	Solution	Composition— g./l. av. oz./gal.	Current Density— Amp./ sq. ft.	Temp. (°C)	Remarks
1. <i>Cathodic cleaner</i>	Trisodium phosphate	15	20	100	Two minutes in this solution produced clean material; longer immersion is likely to cause stains. Iron anodes used.
	Sodium carbonate	15			
	Sodium metasilicate	7.5			
	Sodium hydroxide	3.8			
	Small amount of liquid soap	0.1			
2. <i>Acid pickle</i>	Hydrochloric acid (22 Bé)	180	24	20-30	Two minutes in this solution was found to be sufficient. 180 g./l. is equivalent to 150 cc/l. or 19.6 fl. oz./gal.
3. <i>Copper strike</i>	Basic copper carbonate	27.6	3.7	80	Used by Mathers and Gilbertson. Copper anodes used. Current passed for 15 sec. at current density given.
	Sodium cyanide	57.0	7.65		
	Sodium carbonate	2.6	0.35		
4. <i>Copper plating bath, Rochelle salt type</i>	Cuprous cyanide (CuCN)	30	4.0	60-70	Agitation by moving cathode, overall velocity 5 ft./min. Recommended pH (colorimetric) approx. 12.2. 60 min. at current density will deposit approx. 0.001" of copper. Electrolytic copper anodes used.
	Sodium cyanide (NaCN)	38	5.0		
	Rochelle salts (NaK <sub>2</sub> C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> · 4H <sub>2</sub> O)	45	6.0		
	Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )	30	4.0		
5. <i>Nickel strike (Wood's bath)</i>	Nickel chloride (NiCl <sub>2</sub> · 6H <sub>2</sub> O)	240	32	20-30	145 g./l. of hydrochloric acid is equivalent to 123 cc/l. or 16 fl. oz./gal. Depolarized nickel anodes used.
	Hydrochloric acid (22 Bé.)	145	19.5	(Room)	
6. <i>Silver strike</i>	Silver cyanide (AgCN)	6.5	0.9	20-30	0.9 av. oz./gal. is equivalent to 0.8 tr. oz./gal. Potential should be on electrodes while introducing work into bath. Iron anodes used.
	Potassium cyanide	68	9.0	(Room)	





### (b) Cleaning and Plating Solutions Used

The various cleaning and plating solutions, and normal operating conditions, are given in Table 2. Unless otherwise indicated, the plating cycle generally used at the Bureau of Standards involved: degreasing in trichloroethylene vapor degreaser, and treatment in solutions 1, 2, 4, 6 and 8 in sequence. When a nickel undercoat between copper and silver was called for, solution 5 was often used following solution 4. The work was never allowed to dry, once the sequence had started, and current was always on when the object being plated was lowered into the plating baths.

### (c) Porosity Tests

Three methods were considered for testing the porosity of coatings on steel: the ferroxyl, the salt spray, and the hot-water tests.

(1) The ferroxyl test makes use of an aqueous solution of sodium chloride as a corroding medium. The ferrous ions brought into solution react with the ferricyanide present in the test solution to form ferrous ferricyanide, Turnbull's Blue. The test solution may be applied by means of paper impregnated with the reagent, or as a gelatin solution which congeals and, by preventing diffusion of the corrosion products, localizes the blue precipitate at the pore in the deposit of copper, nickel or silver, as the case may be. In 1934, Strausser, Brenner, and Blum<sup>1</sup> found that this reagent attacks nickel appreciably at the concentrations previously employed, and proposed the use of a more dilute reagent, containing 60 g./l. of sodium chloride and only 0.5 g./l. of potassium ferricyanide.

It was found that even this dilute reagent attacks silver, producing pin-hole perforations in fine silver foil 0.001 inch thick within thirty minutes. Consequently, the ferroxyl reagent, as ordinarily used, is not suitable for testing the porosity of very thin silver coatings, because it might indicate porosity where none existed before making the test. To eliminate attack by the ferricyanide it was suggested by P. W. C. Strausser<sup>2</sup> that the test paper be impregnated with the sodium chloride solution only and, after having been applied to the electroplated specimen, it be immersed in a ferricyanide solution to develop blue spots where the test paper had absorbed iron salts through the pores.

This test is referred to as the "print modification" of the ferroxyl gel test. When the test was made with a gel, it is spoken of as the ferroxyl gel test; otherwise, as the ferroxyl-impregnated paper test.

In the current work, porosity was usually determined by the ferroxyl gel test, using solution 13 of Table 2. This procedure was quite satisfactory where the silver coating was 0.001 inch (0.025 mm) thick and the time of contact with the gel was limited as indicated. For the thinner coatings, if the test proved negative, the silver was considered free from pores extending to the steel beneath, and it appears possible to use this

test judiciously on fairly thin coatings of silver. The sample of plated material being tested was covered with a thin layer of the warm solution, which congealed quickly to a transparent gelatinous film on the surface of the colder metal. The appearance of a blue coloration in less than two minutes signified the presence of iron, thus indicating either a pore in the coating, or superficial iron contamination from the surface of a ferrous die or tool used in a prior forming operation. Material formed was scoured with a mixture of soap and pumice and re-tested, in order that superficial contamination could be distinguished from genuine porosity.

For detecting pores in silver on copper, ferrocyanide is used—or added to the regular ferricyanide solution—as copper reacts with the ferrocyanide to produce a reddish brown precipitate. Solution 13, containing both ferri- and ferrocyanide was used to detect copper or iron exposed beneath a silver deposit because of pores in the silver coating.

Table 3.—Effect of an Intermediate Undercoat of Copper on the Forming Properties, Adherence, and Porosity of Silver-Plated Steel.

Mark	Thickness (in.)		Forming <sup>2</sup>	Adherence <sup>2</sup>	Porosity <sup>1</sup> Pores/sq. dm
	Copper	Silver			
B51	0.0001	No Silver	OK	OK	84-28
B46	0.0001	0.00001	OK	OK	4-4
B47	0.0001	0.0001	OK	OK	2-1
B14	0.0001	0.0002	OK	OK	4-3
B15	0.0001	0.0005	OK	*	12-8
B16	0.0001	0.001	OK	OK	3-0
B52	0.0003	No Silver	OK	OK	76-19
B45	0.0003	0.00001	OK	OK	1-0
B27	0.0003	0.0001	OK	OK	1-0
B26	0.0003	0.0002	OK	OK	2-2
B43	0.0003	0.0005	OK	OK	0-0
B44	0.0003	0.001	OK	OK	0-0
B53	0.0005	No Silver	OK	OK	9-32
B42	0.0005	0.00001	OK	OK	0-0
B22	0.0005	0.0001	OK	OK	2-0
B38	0.0005	0.0002	OK	OK	0-0
B39	0.0005	0.0005	OK	OK	0-0
B21	0.0005	0.001	OK	OK	1-0
B54	0.0009	No Silver	OK	OK	0-10
B31	0.0009	0.00001	OK	OK	0-0
B32	0.0009	0.0001	OK	OK	0-0
B30	0.0009	0.0002	OK	OK	0-0
B33	0.0009	0.0005	OK	OK	0-0
B34	0.0009	0.001	OK	OK	0-0

\*B15 deposit was blistered on one side; this side showed poor adherence.

<sup>1</sup> Hot-water test, front and back surfaces respectively.

<sup>2</sup> OK = Satisfactory.

(2) In the salt-spray test, the specimen is exposed in an enclosed space to a fine mist of a 20 per cent sodium chloride solution. On very thin porous coatings this test was of little value, because the rust was so widespread that individual pores could not be counted. Silver is somewhat soluble in aerated strong brine, and consequently this test

may also indicate pores, as a result of direct attack on thin silver coatings, where none may have originally existed. On thicker coatings with low porosity, the number of pores detected was comparable with, but slightly less than, the number revealed by the ferroxyl test. Owing to the time and equipment involved in extensive salt spray tests, they were discontinued after their general correlation with the other tests had been established.

Table 4.—Effect of an Intermediate Undercoat of Nickel on the Forming Properties Adherence, and Porosity of Silver-Plated Steel.

Mark	Thickness (in.)		Forming <sup>2</sup>	Adherence <sup>2</sup>	Porosity <sup>1</sup> Pores/sq. dm
	Nickel	Silver			
B59	0.0001	No Silver	OK	OK	16-2
B60	0.0001	0.00001	OK	NG	275-100
B61	0.0001	0.0001	OK	OK	72-116
B62	0.0001	0.0002	OK	NG	2-8
B63	0.0001	0.0005	OK	OK	2-15
B64	0.0001	0.001	OK	OK	4-6
B65	0.0002	No Silver	OK	OK	10-3
B66	0.0002	0.00001	OK	NG	48-45
B67	0.0002	0.0001	OK	OK	250-225
B68	0.0002	0.0002	OK	OK	14-27
B69	0.0002	0.0005	OK	OK	13-4
B70	0.0002	0.001	OK	OK	2-7
B71	0.0005	No Silver	Cracked	OK	0-0
B72	0.0005	0.00001	Cracked	OK	2-4
B73	0.0005	0.0001	OK	OK	200-175
B74	0.0005	0.0002	OK	OK	225-150
B75	0.0005	0.0005	Cracked	NG	25-60
B76	0.0005	0.001	Cracked	NG	6-13
B77	0.001	No Silver	OK	OK	0-8
B78	0.001	0.00001	Cracked	NG	2-4
B79	0.001	0.0001	Cracked	NG	33-61
B80	0.001	0.0002	Cracked	NG	16-15
B81	0.001	0.0005	Cracked	OK	2-7
B82	0.001	0.001	OK	OK	0-0

<sup>1</sup> Hot-water test, front and back surfaces respectively.

<sup>2</sup> OK = Satisfactory. NG = Unsatisfactory.

(3) In dealing with very thin deposits of nickel or silver on steel, the ferroxyl gel test, as has been pointed out above, may give misleading results because the reagent attacks these metals to some degree. Consequently, in porosity studies involving such coatings, a hot-water test<sup>3</sup> was preferred. The degreased specimens were heated in distilled water in an open glass vessel at 194-203 °F (90-95 °C) for three hours and allowed to remain in the water, as it cooled, for at least eighteen hours longer. The rust spots developed in this test are readily counted and indicate pores in the coating.

Porosity is reported as the number of pores per square foot or per square decimeter. One square foot corresponds to approximately ten square decimeters, and one pore per square decimeter corresponds to approximately ten pores per square foot. The figures given in Tables 3

and 4 are derived from the number of rust spots counted on the two sides of samples 8×8 inches (20×20 cm) cut from steel of lot 5. Section 3 of this chapter is devoted to a discussion of porosity studies.

#### (d) Formability and Adherence Tests

The *formability* of the plated material was studied by noting the effect of altering its shape and dimensions, using several test methods as outlined below, and discussed in Section 4.

(1) Laboratory tests in which a circular test-piece  $2\frac{5}{8}$  inches (66 mm) in diameter was pressed into the shape of a cup approximately  $1\frac{1}{2}$  inches (38 mm) in diameter and  $1\frac{1}{2}$  inches (38 mm) in depth. The tools used in this test are illustrated in Figure 2. The material under test was considered to form satisfactorily if the cups could be produced without any cracking of the steel or coating. This test also served to test the adherence of the coating, which was considered satisfactory if no peeling occurred.

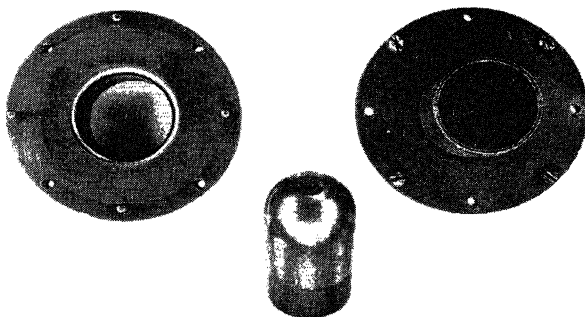


FIGURE 2. Forming tools used in tests on forming properties and adherence of electrodeposited coatings.

(2) Commercial press-forming operations, in which samples of plated material were formed in coöperating industrial plants. In one plant, circles 23 inches (548 mm) or 30 inches (762 mm) in diameter were cold-formed into half-barrel shells such as those shown in Figure 3. The circles were pressed into a simple cup-shape in a single operation, were then expanded to give a taper to the side wall, and subsequently trimmed and perforated as required. By having the silver-coated side of the circle uppermost, facing the mandrel, in effect a silver lining was obtained as a result of the pressing operation. The forming was considered satisfactory only if the plated circles behaved as well as unplated circles under the conditions outlined. The adherence was considered satisfactory if no peeling or stripping of the coating, or any layer thereof, occurred. As

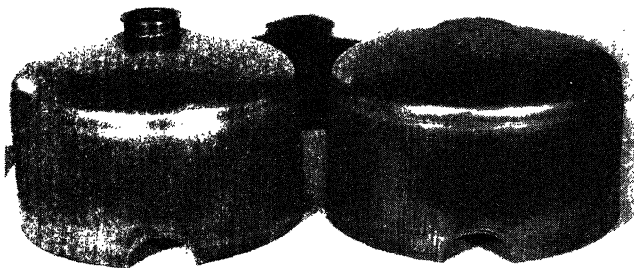


FIGURE 3. Silver-lined half-barrel shells formed from 23"-diameter silver-plated steel circles.

the edges of the shell were cut off in the trimming operation, any tendency for the coating to be held in place mechanically (as a non-adherent liner) could be detected if such were the case. In other plants containers such as the cans and ointment boxes shown in Figure 4 were formed. The can with the cone-shaped top is of particular interest as it is formed by an exceptionally severe deep-drawing operation. The criteria for formability and adherence were the same in these instances as for the barrel shells.

(3) *Rolling of silver-plated steel.* In these tests, samples of plated steel were reduced in thickness and increased in length by passing them

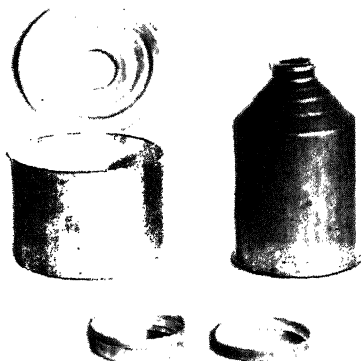


FIGURE 4.

Silver-lined containers formed from electroplated steel sheet (0.001" Ag, 0.001" Cu undercoat).

Upper left: Can body and lid.

Upper right: Can body, seamless drawn.

Lower center: Ointment box and lid.

repeatedly between the polished rolls of a 5-inch rolling mill. Forming was considered satisfactory if no separation of the coating occurred.

(4) *Spinning of silver-plated steel.* Arrangements were made to have samples of silver-plated steel of deep-drawing quality, lot 5, spun into

saucer and goblet shapes. Visual examination served to detect any separation of the plated coating.

(5) *Heating Tests.* (a) In connection with some of the forming tests, attention was given to the effect of heating the plated steel inside a muffle furnace, both in oxidizing and in non-oxidizing atmospheres. The effect of heating on the adherence was noted by bending test-pieces back and forth to fracture through an angle of 180 degrees. The adherence was considered excellent if no separation of the coating could be detected by the bend test or by cold-rolling. The adherence was considered good if the coating withstood cold-rolling even though it could be stripped, at least in part, by inserting a penknife at the point of fracture after the bending test.

(b) Silver-brazing operations, in which plated steel shapes or fittings were joined together by using corrosion-resistant, low-melting silver brazing alloys, served the dual purpose of providing data both on fabrication possibilities and the effect of heating. Although no deformation of the coating was involved in such experiments, the temperatures attained were high enough to reveal any tendency of the coating to strip off, because of differences in respective coefficients of expansion. Oxidation effects, discussed subsequently at some length, were also noted. The result attained was considered satisfactory if the brazed joint possessed the necessary mechanical strength and pressure tightness, and if the integrity of the silver coating was preserved (making due allowance for the narrow strip of brazing alloy exposed at the joint).

#### (e) Embrittlement Tests

The embrittlement of steel produced by the plating operations reported in Section 6 of this chapter was studied by taking samples of steel of lot number 5 at appropriate stages in the plating cycle and comparing the Erichsen value of the selected sample with that of a control specimen. The Erichsen value is the depth, in millimeters, of the cup formed by the spherical mandrel of the Erichsen machine at the moment of rupture or cracking of the cup. A high value is indicative of a high degree of ductility or formability, and a low value indicates poor ductility.

#### (f) Plating at High Current Density

The possibility of plating silver at relatively high current density was studied in an apparatus of special design depicted diagrammatically in Figure 5. Details of the procedure and apparatus used are given in Section 5 of this chapter.

### 3. Porosity of Electrodeposited Silver

#### (a) General

Hothersall and Hammond<sup>4</sup> have presented an excellent picture of the causes of porosity in electrodeposited coatings. The porosity of electro-

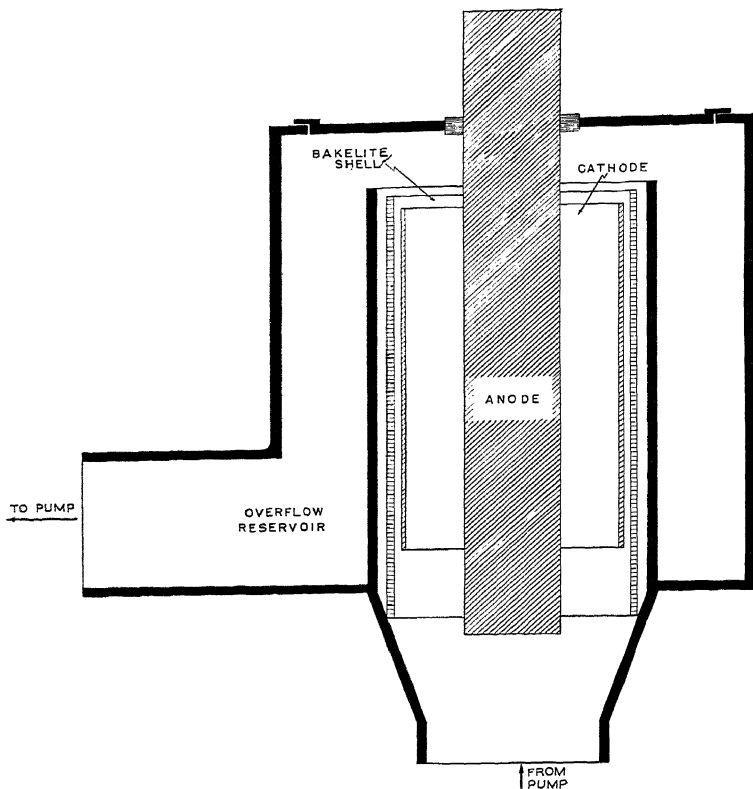


FIGURE 5. Apparatus for plating at high current density.

deposited silver, especially of deposits on steel, has been studied by Mathers and Gilbertson<sup>5</sup> and also by Dornblatt, Lowe and Simon.<sup>6</sup> The latter authors, as well as Strausser<sup>2</sup> have compared methods for testing porosity. A review of some of the more important results obtained and conclusions reached by the silver research fellows at Indiana University and the National Bureau of Standards follows:

**(b) Effect of Surface Finish**

Preliminary studies conducted by C. S. Lowe, using 4×6 inch (100×150 mm) specimens of steel from lot 4, had shown that normal variations in cleaning, pickling, degree of agitation, current density, and temperature had no significant effect on the approximate thickness required for the production of pore-free deposits. He did note that over-

pickling caused increased porosity, and this focused attention on the effect of surface roughness discussed below in some detail.

Mathers and Gilbertson, in their paper on "Porosity of Electro-deposited Silver on Steel"<sup>5</sup> report the results of an investigation to determine the order of coating thickness that might be expected to protect steel not specially prepared or selected for plating. They used hot-rolled and pickled mild steel, acid-detinned tin plate, and polished steel base metals. The sheet produced by dissolving the tin off of tin plate had the roughest surface of the metals studied; the data obtained are probably not representative of results that would be obtained using commercial black (untinned) sheet such as lot 4. The hot-rolled steel surface was intermediate in roughness between the acid-detinned tin plate and the polished steel. Their specimens were 2×2 inch (50×50 mm). Porosity was measured by the ferroxyl gel test. Table 5 gives a summary of the data obtained.

Table 5.—Thickness of Deposit Required for Pore-Free Silver Coating on Steel\*.

Base Metal	Thickness of Silver to Give Zero Porosity		Remarks
	inch	mm	
Detinned tin plate	0.0075	0.190	Plated without silver strike
Hot-rolled steel	0.0060	0.152	Plated without silver strike
Polished steel	0.0010	0.025	Plated without silver strike
Hot-rolled steel	0.0003	0.008	Plated after silver strike

\*Based on data of Mathers and Gilbertson.<sup>5</sup>

The steel of smoothest surface required the least thickness of silver for zero porosity, and the steel with the roughest surface required the greatest thickness of silver. A substantially heavier deposit was needed for equal protection of the metal of poorer surface finish. The use of a silver strike undercoat reduced the thickness of silver coating needed for zero porosity on a given surface.

The observations with respect to the effect of surface finish have been confirmed by work carried out at the Bureau of Standards in the Silver Project's pilot plating plant. The data of Table 6 summarize the results obtained on a large number of specimens prepared for commercial forming tests. Of 218 large flat pieces plated, 75 per cent showed no pores by the ferroxyl gel test, and 89 per cent had fewer than 3 pores per square foot. As many as 58 pore-free sheets were produced in sequence when the baths and work were in proper condition. The data reported and this fact indicate that a properly designed commercial installation should operate with an extremely small proportion of pieces exhibiting any porosity.

The effect of surface roughness on porosity is indicated by the smaller percentages of pore-free coatings obtained on the relatively rougher surfaces of the pickled-finish steel than were obtained on the bright-finish steel sheets of similar analysis, equal thickness of silver, and somewhat



less thickness of copper undercoat. Experience gained in the preparation of many silver-plated circles and sheets taught that if the surface of the steel was particularly rough, scratched or pitted, 0.001 inch or 0.002 inch (0.025-0.05 mm) of copper was not enough to give a pore-free undercoat upon which to deposit the silver. Such material can be detected and rejected before plating, provided the inspector has had sufficient experience to guide him. Even an inexperienced observer could discern that the 30-inch circles were inferior in surface finish to the 23-inch circles from a different shipment; and these in turn were inferior in this respect to the bright finish steel. The porosity data are consistent with this observation.

Table 6.—Porosity Data on Material Plated in Pilot Plant.

Material Plated	Coating Note	Total No.	Total Area Plated		Pore-free Coatings		Not Over <sup>1</sup> / <sub>3</sub> pores/ft. <sup>2</sup> avg.	
			sq. ft.	sq. dm.	No.	%	No.	%
Pickled finish deep-drawing steel 23" diameter circles	1	100	288	2670	74	74	89	89
Pickled finish deep-drawing steel 30" diameter circles	1	50	246	2290	25	50	39	78
Bright finish deep-drawing steel 26"×26" sheets	2	60	282	2620	58	96	58	96
Bright finish deep-drawing steel 26"×26" sheets	3	8	38	350	6	75	8	100
All material		218	854	7930	163	75	194	89

1. Rochelle salt cyanide copper (Solution 4), .0015-.0020", Wood's nickel strike (Solution 5), silver strike (Solution 6), .0010" cyanide silver (Solution 8).

2. Rochelle salt cyanide copper (Solution 4), .0010", silver strike, .0010" cyanide silver.

3. Rochelle salt cyanide copper (Solution 4), .0010", silver strike, .00010" cyanide silver.

4. All material tested for pores extending through to the steel by flooding the surface with ferroxyd gel.

5. One pore/3 dm<sup>2</sup>.

Laboratory experiments conducted at the Bureau had also indicated that the thickness of deposit required for zero porosity increases with roughness of the steel surface. It was for this reason, as well as for other considerations, that a substantial undercoat of copper was used before attempting to deposit the silver on steel, where pore-free silver was required. No significant difference in porosity was noted where the steel had a reasonably clean and smooth surface and where the deposit was thick compared to the depth of surface irregularities or marking. Thus, as shown in Table 7, if the silver was as much as 0.0005 inch thick, a low order of porosity was obtained on steel of lot numbers 3, 4, 5, and 7. It is reported <sup>7</sup> that a sample of steel of lot 7, examined by a profilometer, showed maximum surface irregularities of 0.000003 inch (0.000075 mm). Ordinary cold-rolled steel will exhibit much larger irregularities of profile.

While it is possible that the difference in finish between cold-rolled, bright finished material, and polished material of the same composition and inherent cleanliness may influence the porosity of coatings thinner than a half-thousandth inch, it is doubtful if silver coatings less than 0.0005 inch (0.0125 mm) thick, directly deposited on steel, are of commercial significance. Galvanic corrosion between silver and steel is so serious that the silver coating to be used will either be much thicker, or else an undercoat such as electrodeposited copper will be used. Upon this undercoat 0.0001 inch (0.0025 mm) of silver, and possibly less, can be deposited without pores extending through to the copper. Table 6 records zero porosity for six sheets 26×26 inches (660×660 mm) which have 0.0001 inch of silver over a copper undercoat on bright-finish steel.

Table 7.—Variation of Porosity With Surface Quality of Base Metal  
Porosity\*, Pores/Dm<sup>2</sup>.

Silver Deposit (inches)	Mirror Finish, Steel No. 7	Satin Finish, Steel No. 3	Bright Finish, Steel No. 5	Mill Finish, Steel No. 4	Mirror Finish, Copper No. 8
.00001	**	—	**	**	12
.0001	66	—	86	290	1
.0002	100	67	72	96	0
.0005	10	4	0	1	0
.001	3	0	0	9	0

\*Hot Water Test used on steel samples, Ferrocyanide-impregnated paper used on copper samples.

\*\*Too numerous to count.

It may be concluded from the above that the thickness of silver deposit required for zero porosity depends on the surface finish of the base metal, being greater for rougher surfaces. This conclusion is not restricted to electrodeposits of silver, but is a general conclusion applicable to the total thickness of any electrodeposit or combination of metals in the deposit. No doubt the minimum thickness required to produce a pore-free deposit on a surface of given finish also depends on the chemical nature and homogeneity of the base metal. Non-metallic inclusions in the base metal may affect the porosity, since, being non-conductors, the metal does not deposit upon them, but must bridge over them if they are to be covered at all. Metals vary widely in respect to freedom from such inclusions and in "cleanliness." Voids and fissures must also be considered as factors influencing porosity. It is obvious that an electrodeposited metal is itself an excellent example of a material of comparatively great chemical purity and homogeneity, and therefore an excellent base upon which to deposit pore-free coatings of minimum thickness, always provided that the under coat has a good surface finish.

### (c) Effect of Undercoats

It is of interest to know just how the porosity of a silver deposit is influenced by electrolytic undercoats. Experiments were conducted with this point in mind, and the effect of copper and of nickel undercoats

determined. The results are given in Tables 3 and 4 (pp. 249 and 250). (The effects of the undercoats on forming properties and adhesion are discussed later.)

It will be noted that, with this bright-finish steel, pore-free deposits were obtained with 0.001 inch (0.025 mm) of silver on either 0.0009 inch (0.023 mm) of copper or 0.001 inch (0.025 mm) of nickel. A low porosity was obtained with a copper undercoat only 0.0003 inch (0.0075 mm) thick and silver 0.0001 inch (0.0025 mm) thick. The nickel undercoats were less effective than copper, and were not entirely pore-free, even if 0.001 inch (0.025 mm) thick. Subsequent experience has shown that thinner pore-free deposits of copper or nickel can be produced on this grade of steel,\* but the general conclusion that a copper undercoat of a given thickness is preferable to nickel remains unchanged.

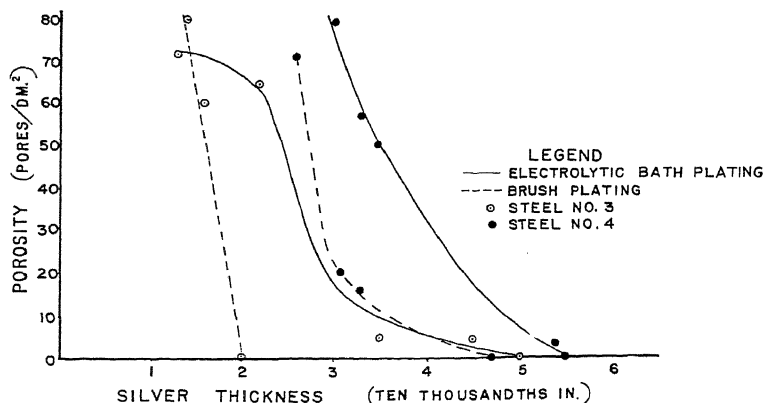


FIGURE 6. Variation of porosity with base metal, thickness and plating method. Porosity by FerroxyI impregnated paper.

#### (d) Effect of Method of Plating

Mathers and Gilbertson<sup>5, 8</sup> describe experiments using the method of "sponge" or "brush" plating. Silver was plated directly upon hot-rolled steel and deposits were obtained which showed no porosity with 0.0003 inch (0.007 mm) of silver.<sup>5</sup> Bath-plated silver, deposited upon the same grade of steel after a silver strike required the same thickness of silver for zero porosity. However, bath-plated steel plated without the use of a silver strike required a much heavier silver deposit to achieve zero porosity. Figure 6 shows the variation of porosity with base metal,

\* As work progressed, the connection between porosity and suspended matter in the bath impressed itself upon those conducting the investigations, with the result that more complete elimination of such particles by careful and frequent filtration led to better results, with respect to freedom from porosity, in the later stages of porosity studies.

thickness, and plating method as determined by Dornblatt, Lowe and Simon.<sup>6</sup> The figure shows that for the particular steel used, brush-plated coatings gave a lower order of porosity than did conventional bath-plated coatings. Mathers and Gilbertson<sup>5</sup> found that, when the brush-plated cathodes were replated in the bath to 0.01 inch (0.25 mm) thickness and tested for adherence, in no case was the adherence of the deposit on the brush-plated cathodes as good as that on the bath-plated cathodes. Brush-plated silver tended to bridge over the larger pits in the steel surface, whereas the bath-plated silver tended to follow the contour of the metal surface more closely, and thus obtained a better anchorage.

It seems possible that brush plating is less influenced by suspended matter in solution than still or bath plating, as the mechanical action of the brush sweeps away particles that might produce porosity.

### (e) Technique Required to Produce Pore-free Coatings

The production of thin but pore-free deposits of copper or silver on steel does not require procedure radically different from commercial plating practice. It depends on three chief factors, namely: (1) the selection of a steel of suitable surface quality; (2) proper cleaning before plating; and (3) maintenance of a nearly optically clear \* electrolyte, free from suspended solids. The bright-finish steel used in these experiments is a relatively recent development. The availability of this material at low cost and in various gauges should be a boon to the electroplater and the users of electroplated steel, particularly those interested in material to be formed after plating. Careful visual inspection will serve to indicate surface flaws, and inferior material should be rejected before undertaking any plating. In the absence of a base metal of relatively smooth (not necessarily bright) surface and of good quality with respect to non-metallic inclusions and surface flaws, it becomes necessary to apply a heavier deposit to compensate for poor surface quality of the base metal.

An electrolytic copper undercoat serves to provide a homogeneous material upon which a thin coating of silver can be deposited with a minimum likelihood of porosity; furthermore, a substantial part of the total thickness required is a low-cost metal, thus conserving silver. The freedom from progressive corrosion by galvanic action if copper is exposed beneath the silver, as by mechanical abrasion, also makes it very suitable for an undercoat. Other electrodeposited metals may, however, be substituted if the circumstances so warrant.

The second factor is broad enough for volumes to be written about it, and further discussion is beyond the present scope. The third factor is a matter now being given much attention in connection with commercial bright nickel-plating. The efficient filtration of plating solutions, despite

\*In an optically clear solution, a focused beam of light passing through the solution is not visible when viewed at right angles to its path. When even minute particles are present, they will be visible like motes of dust in a sunbeam.

considerable progress, is still beset with problems, which should challenge the interest of enterprising chemical engineers.

In the pilot plant work it was noted that, once the baths were working properly and a suitable steel was in the copper bath, the chief source of difficulty was the formation of loosely adherent nodules upon the surface of the freshly deposited copper. Silver deposited on such a coating was particularly porous. In some instances these nodules, on being dislodged, exposed bare steel at the bottom of the depression formed around the nodule by the electrodeposit. It was found that, if the bath temperature was closely controlled and the cathodes scrubbed with pumice to remove the nodules after each half-thousandth inch of copper was deposited, it was easy to obtain copper coatings 0.001 inch (0.025 mm) thick which were pore-free over their entire area.\* As has been remarked above, silver coatings as thin as 0.0001 inch (0.0025 mm) can be deposited upon such a foundation in a pore-free condition.

The authors' experience indicates that anodes of highest purity, surrounded by suitable anode bags, should be used to minimize the introduction of solid matter from the dissolution of the anodes; that filtration be continuous or frequent; that tanks be kept covered to exclude dirt and dust (air conditioning of the plating room is recommended); and that, if necessary, the cathodes should also be bagged. Care must be taken in using siliceous filter aids, because silicates may be formed in the alkaline solutions.† Siliceous flakes have been observed in a silver bath several days after filtration. Continuous filtration may do more harm than good if it merely keeps solid matter in suspension. It should be so used as to keep the solutions clarified, and not to reduce the content of sludge in a badly contaminated solution.

#### 4. Forming of Silver-plated Base Metal

##### (a) Adherence

(1) *Indiana University Fellowship Results on Adherence of Thick Silver Plate on Steel.*—Mathers and Gilbertson, in their paper, "The Adherence of Thick Silver Plate on Steel"<sup>8</sup> explore the possibility of depositing silver several hundredths of an inch thick on steel, with the idea of producing silver-lined bearings by electrodeposition. Because of the service conditions anticipated, the bond between the silver and the steel must be excellent.

Also, since the silver lining was to be of maximum purity, it was desirable to avoid the use of an undercoat, such as copper, which might simplify the bonding problem but introduce some contamination of the silver if diffusion of the copper occurred at the elevated temperatures

\* It is important that great care be taken to remove all the pumice by scrubbing while rinsing, as otherwise some particles will adhere despite rinsing, and will cause the formation of nodules of the type under discussion.

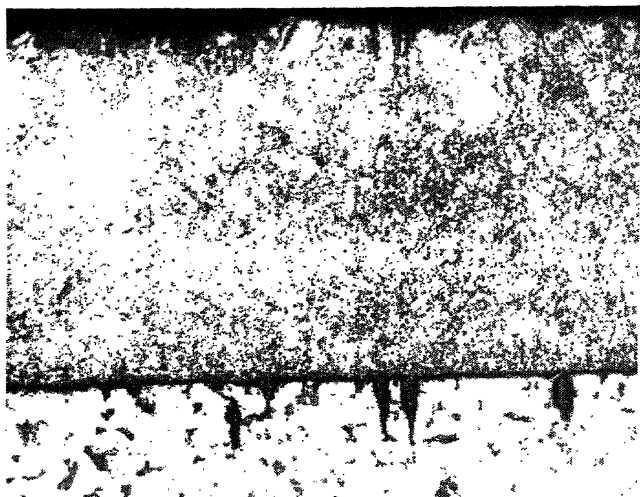
† Glass fiber anode bags are not beyond suspicion for the same reason.

encountered in aviation bearing service. Nickel might also have been used, but, for the reason above, the work was devoted primarily to a study of methods for obtaining the desired bond and thickness by direct deposition of silver. These authors described recommended conditions for cleaning, pickling, striking, and silver plating iron and steel. The properties of thick silver plate were also discussed.

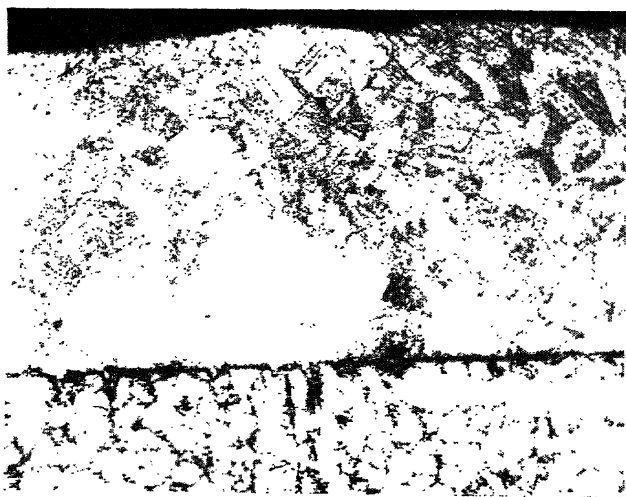
Typical conditions recommended by Mathers and Gilbertson will be reviewed briefly. Vapor degreasing, or alkaline degreasing, must be followed by an acid dip. For pickling mild steel, the acid dip might be 15 seconds in 10-per cent hydrochloric or sulfuric acid, at 90 °C.

For higher-carbon steel, after degreasing and acid dipping, electrolytic cleaning is preferable, using 80-per cent sulfuric acid as an anodic cleaner operating at 200 amperes per square foot (20 amp/dm<sup>2</sup>), or 10-per cent hydrochloric or sulfuric acid as cathodic cleaners at 100-200 amperes per square foot (10-20 amp/dm<sup>2</sup>). The strike bath listed as solution 7 in Table 2 (p. 246) is next used, taking precaution to avoid permitting the freshly cleaned surface to become dry at any time between the acid dip and final plating, and also arranging to have the current on at the instant the cathode is introduced into the strike bath. Plating to the desired thickness in solution 9 of Table 2 completes the plating cycle. Gentle agitation to prevent layer formation, and also frequent or continuous filtration are recommended adjuncts for the production of an even, fine-grained deposit. Note that intermediate buffing was not used in building up coatings as thick as 0.05 inch (1.3 mm). Microscopic examination will show that interrupted deposition with intervening buffing and polishing results in a stratified deposit, which may peel or separate between layers under severe service conditions. Thick deposits tend to become nodular and irregular as they get thicker, but the use of a low current density and carefully filtered electrolyte will reduce the tendency to rough deposits, and an uninterrupted deposition will eliminate trouble due to stratification of the sort mentioned.

Mathers and Gilbertson observed that adherence was adversely influenced by the following factors: presence of, or incomplete removal of, oxide films formed by even brief exposure of the cathode to oxygen from the air, or by action of alkaline cleaners; presence of traces of grease; insufficient pickling or etching; failure to have the cathode connected to the current source before immersion in the strike. The apparent adhesion of the silver coating is affected by thickness, *e.g.*, a thin deposit of imperfect adhesion is noticeably poorly adherent after a heavier coating has been built up on this thin coating. As the thicker deposit lends itself more readily to mechanical testing of the bond than does the thin deposit, and as the stresses in the coating as deposited are probably greater in magnitude in the thicker deposits, this behavior is to be expected. Where the adhesion of the thin deposit was excellent, subsequent building up of the deposit did not reduce the adhesion of the



As deposited.  $\times 100$ .



Annealed at 1400 °F.  $\times 100$ .

FIGURE 7. Electroplated silver on steel.

coating to the steel. Heating the electroplated specimens for one hour at 1000 °F (538 °C) was found to improve the adherence of poorly adherent coatings. In a few instances blistering and reduced adherence, attributed to occlusion of electrolyte or hydrogen gas, accompanied the annealing. The photomicrographs of Figure 7 show the structure of the electrodeposited silver before and after annealing at 1400 °F (760 °C) for 10 minutes. The degreased specimen of 0.1 per cent carbon steel had been treated cathodically in 10-per cent hydrochloric acid at 90 °C and 10 amp/dm<sup>2</sup> for two minutes, after which it was given a silver strike using solution 7, and coated with 0.03 inch (0.76 mm) of silver from solution 9. The coating withstood this drastic heating without any indication of failure at the bond. It is interesting to note that the steel has been etched deeply at the grain boundaries and that the silver has deposited within the crevices thus formed.

These authors found that the desired quality of bond could be obtained with less careful regulation of the time in the strike bath by using a copper strike such as solution 3, Table 2, (p. 246) rather than by using the silver strike. Apparently this was due to the greater ease with which a complete coverage of the cathode could be obtained in the copper strike with less likelihood of "treeing." As will be pointed out later, the present authors believe that the copper coating obtained from a solution such as number 4, Table 2, adheres well to steel, and may be used to deposit a bonding coat at lower current density.

Mathers and Gilbertson<sup>8</sup> state that the silver strike bath should be operated at a current density sufficient to provide vigorous gassing at the cathode during the strike, and the time of the strike should be so regulated as to assure complete coverage of the cathode without any appreciable "treeing" of the strike coat. Otherwise, operating conditions are not particularly critical, and in fact a wide range of strike bath compositions is permissible. Similarly, several different plating baths gave smooth, fine-grained thick deposits. The softest deposits were obtained by Mathers and Gilbertson using solution 9, which is similar to solution 8 used at the Bureau of Standards; the hardest, smoothest, and brightest were obtained from solution 11. The latter deposits were brittle.

(2) *Tests on Adherence and Formability, National Bureau of Standards.*—The tests summarized in columns 4 and 5 of Tables 3 and 4 (pp. 249, 250) were made to note the conditions affecting the adherence of silver coatings on steel. The forming properties and the adherence of the plated material were studied by forming a circle cut from plated stock into a cup with the tools shown in Figure 2 (p. 251). The specimens to be cupped were cut from pieces 8×8 inches (200×200 mm) which had been plated simultaneously with the porosity test specimens. Table 3 shows that where a copper undercoat was used, all samples could be easily formed into cups. In only one instance was the



adherence unsatisfactory, namely, specimen B-15, which exhibited blisters on one side of the plated sheet before forming. Some peeling of this blistered surface was noted after forming.

Table 4 shows that forming was usually unsatisfactory with a nickel undercoat 0.0005 inch (0.012 mm) or 0.001 inch (0.025 mm) thick, as 8 out of 12 specimens cracked. Probably this cracking was caused by hydrogen embrittlement, and did not occur with the thinner nickel coatings because of their shorter time in the nickel-plating bath. The fact that the samples which failed during the forming operations developed cracks after only a very small amount of deformation is indicative of embrittlement rather than failure due to work-hardening a ductile material.

The adhesion of the deposit on many of the specimens with the nickel undercoat was unsatisfactory. From these data it appears that better adherence and formability will generally be obtained with a copper undercoat than with nickel. However, coatings of nickel deposited on steel are known to have withstood forming operations quite successfully, so that the remark above may be strictly applicable only to the particular set of test conditions.

Table 8—Comparison of the Forming Properties and Adherence of Silver-Plated on OFHC Copper and Bright-Finish Steel.

OFHC Copper				Bright-Finish Steel			
Mark	Silver Thickness (inch)	Forming Adherence		Mark	Silver Thickness (inch)	Forming Adherence	
		No Acid Pickle				No Acid Pickle	
C1-1A	0.00001	OK	OK	B1-1A	0.00001	OK	OK
C2-1A	0.0001	OK	OK	B2-1A	0.0001	OK	OK
C3-1A	0.0002	OK	OK	B3-1A	0.0002	OK	OK
C4-1A	0.0005	OK	OK	B4-1A	0.0005	OK	NG
C5-1A	0.0010	OK	OK	B5-1A	0.0010	OK	NG
C6-1A	0.0010	OK	OK	B6-1A	0.0010	OK	NG
5 Min. Acid Pickle				5 Min. Acid Pickle			
C7-1A	0.00001	OK	OK	B7-1A	0.00001	OK	OK
C8-1A	0.0001	OK	OK	B8-1A	0.0001	OK	NG
C9-1A	0.0002	OK	OK	B9-1A	0.0002	OK	OK
C10-1A	0.0005	OK	OK	B10-1A	0.0005	OK	NG Outside
C11-1A	0.0010	OK	OK	B11-1A	0.0010	OK	OK Inside
							OK Outside
							NG Inside

NOTE:—OK = Satisfactory. NG = Unsatisfactory.

Table 8 presents a comparison of the forming properties and adherence of silver plated on polished, oxygen-free, high-conductivity copper and on bright finish steel. The specimens were plated with silver, following a silver strike using solution 6. In one series on steel, no acid pickle was used before the silver strike, in the other series, before the silver strike, the specimens were pickled for five minutes in 22° Bé hydrochloric acid at room temperature. The steel surface was only very lightly etched

by the treatment, which is more mild than the pickle recommended by Mathers and Gilbertson.<sup>8</sup>

The forming and adherence of silver on copper were entirely satisfactory. The forming properties of the silver plated directly on steel were satisfactory, but the adhesion was poor and variable. Specimens B10-1A and B11-1A showed that the adherence was not equal on the two sides of the same piece of steel. While good adhesion might have been obtained with silver plated directly on steel, by the procedure outlined by Mathers and Gilbertson, it was considered more expedient to insure adherence by using the copper undercoat.

### (b) Commercial Forming Tests

Over one hundred circles have been plated as described in Table 7 (p. 257) and pressed hydraulically into half-barrel shells similar to that shown in Figure 3 (p. 252), without a single failure in the adhesion of the electrodeposited coating.

Samples of bright-finish steel sheet plated with 0.002 inch total thickness of deposit as described in Table 7 have been formed into ointment boxes and cans of the types shown in Figure 4 (p. 252) without separation of the coatings. The ability of such coatings to withstand drastic plastic deformation is best illustrated by the can body shown in Figure 4, which was drawn through a set of beer can dies from a flat circle 8 inches (200 mm) in diameter.

Sample containers of these various types have been tested and found pore-free after these forming operations on commercial presses. Misleading results are obtained when testing for exposed iron, unless the forming tools are chromium- or nickel-plated, as the work picks up enough iron from the die to give the blue ferroxyl coloration. It is possible to differentiate between superficial contamination and pores by successive cleaning operations with a mixture of soap and pumice, followed by ferroxyl gel tests to note the persistence of the blue spots in a given locality. However, pumice abrades silver fairly rapidly and its use is not to be generally recommended. The surfaces of the forming tools used for work of this nature should be non-ferrous, clean, smooth, and highly polished.

### (c) Rolling of Silver-plated Steel

Table 9 summarizes tests on the effect of various heat-treatments and of rolling upon the adherence and porosity of silver deposits. All samples given a nickel strike (solution 5) showed perfect adherence of the coating to the steel. These samples (1 to 4) withstood reductions of 50 per cent or more in thickness without any separation of the coating. After a preliminary cold-reduction of 50 per cent and 70 per cent, respectively, annealing of samples 3 and 4 at 1500 °F (816 °C) for  $\frac{1}{2}$  hour in a non-oxidizing atmosphere permitted them to be further reduced. Perfect adhesion was also obtained with sample 7 (plated with copper, nickel

Table 9.—Effect of Heating and Rolling on Adherence and Porosity of Steel Electrolytically Coated with Silver.

Sample No.	Steel *	Coating <sup>1</sup>	Treatment after Plating		Final Silver Thickness (in.)	Adherence	Porosity Pores/dm <sup>2</sup>
			Cold-rolled	Annealed			
1	0.076"	Ni strike 0.0062" Ag	—	1500 °F ½ hr <sup>1</sup>	0.082" to 0.041"	Excellent	None
2	0.076"	Ni strike 0.0062" Ag	—	1300 °F ½ hr <sup>1</sup> then 1500 °F ½ hr <sup>1</sup>	0.082" to 0.041"	Excellent	None
3	0.076"	Ni strike 0.0062" Ag	0.082 to 0.041"	1500 °F ½ hr <sup>1</sup>	0.041" to 0.0203"	Excellent	None
4	0.076"	Ni strike 0.0062" Ag	0.082 to 0.024"	1500 °F ½ hr <sup>1</sup>	0.024" to 0.010"	Excellent	None
5	0.022"	0.005" Ag direct	—	1500 °F ½ hr <sup>1</sup>	0.027" to 0.013"	Good	None
6	0.022"	0.010" Ag direct	—	1400 °F ½ hr <sup>2</sup>	0.032" to 0.004"	Very Good	—
7	0.050"	0.0015" Cu, Ni strike 0.002" Ag	(a) 0.0535 to 0.0175" (b) 0.0875 to 0.0020"	—	0.0018 0.0006	Excellent	None
				—	0.00008	Excellent	400

<sup>1</sup> Non-oxidizing atmosphere.<sup>2</sup> Oxidizing atmosphere.<sup>3</sup> Deep-drawing steel used throughout.<sup>4</sup> Silver strike precedes silver plating in each instance.

strike, silver strike, silver). This is the kind of coating that was used in the preparation of material for silver-lined barrel shells.

Silver plated directly on steel, as in samples 5 and 6, was adherent enough to roll satisfactorily, but some separation of the coating from the rolled sheet could be effected if, after the sheet was fractured, a pen-knife was inserted adjacent to the fracture. The adherence of the silver of sample 5 was noticeably less than that on sample 6, which was heated in an ordinary muffle furnace, exposed to air. The better adhesion produced by this treatment was also evident on the plated and rolled sheet. The surface condition of most of the specimens after final rolling was very good. A few small blisters were noted on some of the heated samples that had been plated on the 0.076 inch (1.93 mm) steel, and these blisters persisted in the rolled material. Other samples from the same original piece of plated steel did not show such blisters under similar treatment. The silver coatings obtained after rolling were pore-free, except when the final thickness of silver was less than 0.006 inch.

These experiments indicate that silver-coated mild steel sheet can be manufactured by electroplating a steel slab with silver and rolling the plated slab to the required length and gauge. The steel, after cleaning, is preferably first treated in Wood's nickel strike bath, after which it receives a silver strike and then the silver deposit. The thickness of the silver deposit is a predetermined fraction of the thickness of the steel slab being plated; and Mathers and Gilbertson have demonstrated that there is no great difficulty in plating 0.07 inch of silver as a single smooth deposit on mild steel. The dimensions of the slab are chosen with due regard to the final sheet dimensions. Intervening annealing, if necessary, must be done in a non-oxidizing atmosphere, unless the silver coating is thick enough to prevent excessive oxidation under the particular operating conditions.

Plating a thick slab of small area, which is subsequently rolled down to a larger area, rather than plating an equivalent sheet of large area has the following advantages: (a) the size of the plating installation required, and thus the investment costs, are reduced; (b) the rolling operation is itself a test of the bond; (c) high physical properties are obtainable; and (d) a smooth and hard surface may be produced. The process lends itself to the preparation of large sheets of silver-coated steel. If the reduction in gauge can be accomplished entirely by cold-working, it may be more economical than attempting to obtain equally large silver-clad sheets by rolling heavy-gauge clad slabs.

#### (d) Spinning

Samples of bright-finish steel number 5, plated with 0.001 inch (0.025 mm) of copper and 0.001 inch (0.025 mm) of silver have been spun into various hollow-ware shapes, such as ash-trays, bowls, and cups without the spinning operation causing any separation of the plated

coating from the steel. It seems that this method might be used to advantage in the manufacture of silver-lined vessels and decorative objects. Brass, copper, nickel-silver or other ductile sheet metal could be used as a base, as well as steel. If steel is used, a suitable organic decorative and protective coat, or some electroplated metal, might be applied to the side of the sheet opposite the silver-coated side.

### (e) The Effects of Heating

(1) *General.*—The effect of heating electroplated metals, with particular reference to the adhesion of the deposit, has been considered by other workers. Hothersall<sup>9</sup> noted an improvement in adhesion of nickel on brass upon heating at a temperature of 212 to 482 °F (100 to 250 °C) for 2 to 4 hours. Mathers and Gilbertson<sup>8</sup> reported an improvement in the adhesion of electrodeposited silver to steel upon heating the material for 1 hour at 1000 °F (538 °C) and prepared steel coated with 0.03 inch (0.76 mm) of silver which withstood heating for ten minutes at a temperature of 1400 °F (760 °C). Mesle<sup>10</sup> called attention to the effect of moderate heating in improving the adhesion of electrodeposits. Ritzen-thaler<sup>11</sup> discusses the effect of heating samples of copper, brass, and bronze sheets electroplated with cadmium, zinc, tin, and nickel. In the discussion of a paper on alloys of silver and iron by Fink and de Marchi,<sup>12</sup> reference is made to the use of a silver coating to protect an engraved steel roll while heating it for hardening in a reducing atmosphere at a temperature of 1600 °F (870 °C) for several hours. The silver coating, although only from 0.0001 to 0.0002 inch thick, sufficed to protect the steel and the delicately engraved design under these conditions. Silver plating has been suggested for protecting die parts to prevent scaling.<sup>13, 14</sup>

It is apparent that under certain conditions heating to moderate temperatures might improve the adhesion. On the other hand, coatings have been known to peel or blister, owing to heat such as that developed in buffing and polishing operations. Evidently, heating of electroplated metals produces opposing effects, which vary in importance, depending on circumstances.

What happens when silver-plated steel is heated is of special concern if it is to be used in brazed assemblies, or if it must be annealed to permit further working of the steel after prior cold deformation.

For example, two of the silver-lined shells, formed by hydraulically pressing silver-coated steel circles into a roughly hemispherical shape, must be joined together to make a leak-proof, barrel-shaped vessel. Fusion welding, the conventional practice, was out of the question, as the thin silver coating would be melted off at temperatures high enough to fuse the steel.\* A brazed lap joint might be used, as there are avail-

\* Silver-clad steel is fabricated commercially by fusion welding, but this is a different situation owing to the ability of a more massive coating of the type used on the clad metal to dissipate the heat of welding.

able silver alloys suitable for brazing steel at temperatures as low as 1175 °F (635 °C) which also possess good resistance to corrosion. Fittings might also be brazed into place. The question arose: Can steel be electroplated so that the silver coating will not be damaged at brazing or annealing temperature? If a coating could be developed to withstand annealing it would be possible to fabricate pressed shapes, coated with silver on one or both sides, that are too large or too complicated to form without an intervening annealing treatment to restore the workability of the steel. Furthermore, large steel slabs might be electrolytically clad with a heavy silver deposit and subsequently rolled to sheet of various gauges. Considerations of this nature led the authors to a detailed study of the effect of heating electroplated coatings, especially of silver.

The above problem of heating silver-plated metals presents several uncommon factors: (1) the silver-plated metal to be joined by brazing is to be subjected to an unusually high temperature; (2) at elevated temperatures silver is permeable to oxygen; and, (3) at high temperatures diffusion alloying may occur if an undercoat is used beneath the silver.

That silver is permeable to oxygen at elevated temperatures can be demonstrated by placing a protective covering over a piece of steel thinly plated with silver in such a manner that part of the plated steel is exposed to the air and another portion remains shielded. A brazing flux\* serves admirably for this purpose. When the steel is heated to a barely visible red heat, blisters develop on that portion of the specimen surrounding the pool of flux, while no blisters develop in the protected area. When the blisters are opened, the film of oxide which forms beneath the silver coating is visible. This experiment is cited to emphasize the fact that, when silver coatings are exposed to relatively high temperatures in an oxidizing environment, there is danger that the underlying metal will be oxidized. If oxidation takes place to any considerable extent, the plating blisters and peels. Whether oxidation actually occurs will depend on the temperature, the time of heating, and the thickness of the coating.

The adhesion of electrodeposited silver to steel is not as good as that of electrodeposited copper to steel under like conditions. However, it has been shown that excellent adhesion of the silver coating is obtainable when a copper undercoat is used. Especially at high temperatures, the copper can readily diffuse into both the silver and the steel and establish a true alloy bond at the respective interfaces. Silver on the other hand has little, if any, tendency to diffuse into the steel, or *vice versa*; hence it is more difficult to get a satisfactory bond directly on steel.

Although the copper undercoat is desirable to secure adequate adhesion of the silver coating, when the coating is heated, the rate of diffusion increases and two undesirable effects may result: (1) a silver-copper alloy may form, which is less resistant to corrosion and may introduce

\* "Handy Flux," sold by Handy & Harman, 82 Fulton St., New York City, is suggested.

copper into the corroding environment; (2) the coating may be destroyed by formation and melting of the copper-silver eutectic at the temperature of 1436 °F (780 °C). Since nickel does not form a low-melting eutectic alloy with silver, and acts as a barrier, retarding diffusion when plated between copper and silver, it seemed advisable to use a thin nickel coat between the silver and copper. Nickel could be used instead of copper as an undercoat between silver and steel, but it is more expensive.

(2) *Experimental Studies.*—To determine the conditions that restrict the heating of electroplated silver coatings on steel, tests were made on the effects of temperature, time, and thickness of the coating upon the performance of silver coatings applied over undercoats of copper, nickel, or copper plus a nickel strike. The effects of heating the coatings in air and in non-oxidizing atmospheres at temperatures ranging from 400 to 1600 °F (204 to 871 °C) for intervals from 5 minutes to 10 days were studied.

The samples used for the tests carried out in an oxidizing atmosphere consisted of pieces 2×2 inches (51×51 mm) cut from steel circles of lot 1, 23 inches (580 mm) in diameter and 0.022 inch (0.56 mm) thick, which had been plated on one side only. A tempering furnace equipped with a circulating fan was used for heating at 400 and 600 °F (204 and 316 °C) and a muffle type furnace was used for higher temperatures. The samples of each plating combination were placed in the furnace when it came to the desired temperature. One sample of each series was removed after each time interval, and was examined for blistering and oxidation beneath the silver deposit.

Tests were conducted in a non-oxidizing atmosphere at 1300 and 1400 °F (649 and 760 °C) by packing the specimens in finely divided graphite, and at 1500 °F (816 °C) by using a furnace with a controlled atmosphere. For the latter tests, some of the original material, having 0.005 inch (0.127 mm) of silver plated directly on steel, was used. Additional material was prepared by using steel of the same quality, applying a nickel strike, using Wood's nickel solution, a silver strike, and then depositing 0.0062 inch (0.16 mm) of silver.

(3) *Results of Experimental Studies.*—(a) *Specimens Heated in an Oxidizing Atmosphere.*—Table 20 summarizes some of the data obtained on the effect of heating silver-plated steel. The table shows that samples having silver plated directly on steel or over a nickel undercoat did not blister when heated to a temperature from 400-1600 °F (204 to 871 °C). Blistering was observed at or above 1200 °F (649 °C) on the samples when copper was used as an undercoat, and at or above 1300 °F (704 °C) when a combination of a copper plus a nickel strike was used as an undercoat. Oxidation was evident beneath the silver on all plating combinations after very short exposures at high temperatures, and after prolonged exposures at low temperatures on all samples except the samples plated with 0.005 inch (0.127 mm) and 0.01 inch (0.254 mm) of silver. These heavier silver coatings offered greater protection to the





steel against oxidation.\* For example, a definite oxidation of the steel was produced by heating at 1200 °F (649 °C) for only 15 minutes where the silver was 0.001 inch (0.025 mm) thick, whereas the same effect was produced in the case of 0.005 inch (0.127 mm) of silver only after 30 minutes, and in the case of 0.010 inch (0.254 mm) of silver, only after 60 minutes. The effect of higher temperatures in promoting oxidation is indicated by the shorter time required to produce oxidation beneath a given thickness of silver at the higher temperature. Again, the time required for definite oxidation to be observed beneath 0.005 inch (0.127 mm) of silver was one day at 600 °F (316 °C), 30 minutes at 1200 °F (649 °C), and only 5 minutes at 1400 °F (760 °C).

The more heavily silver-plated samples had a poor initial adherence. The adherence was improved by short exposures to as low a temperature as 400 °F (204 °C). After heating the samples 30 to 90 minutes at temperatures from 1400 to 1500 °F (760 to 816 °C) a very marked improvement in adherence was observed on the steel samples plated with 0.005 inch (0.127 mm) and 0.01 inch (0.254 mm) silver. This confirms the work of Mathers and Gilbertson.

The general trend of all these results indicates that the permeability of silver to oxygen increases rapidly with increase in temperatures and varies inversely with the thickness.\* The observed improvement in adhesion can be explained by assuming that heating reduces the effect of factors that tend to produce what Hothersall<sup>15</sup> calls "weakness of the surface layer" of the steel. At elevated temperatures, absorbed hydrogen is driven off, and internal stresses, which also tend to produce weakness of the surface layer, are relieved. It also seems possible, in the case of silver-plated steel heated in an oxidizing atmosphere, that there is a bonding between silver and the iron oxide formed, and in turn between iron oxide and iron. This would explain the improved adhesion. When the iron oxide film is thick enough for failure to take place in the film itself the adherence is again reduced. If alloying occurs between the deposit and the base metal, heating tends to improve the bond by favoring alloying through diffusion.

(b) *Specimens Heated in Non-oxidizing Atmosphere.*—No oxidation could take place. No blistering of silver plated directly on steel was observed, but some samples of the silver with the nickel strike undercoat showed small blisters, which may be attributed to inadequacy of the cleaning treatment, or the liberation of absorbed hydrogen upon heating.

The adherence of the specimens prepared with the nickel strike was excellent. The specimens that had no undercoat or nickel strike showed

\* Note the absence of any harmful effect in the case of the sample with 0.03 inch thick silver coating depicted in Figure 7b, after heating ten minutes at 1400 °F (760 °C).

\* The diffusion of oxygen through silver is taken up mathematically in Chapter 18.

good adhesion of the silver coating to the steel, but the coating showed some evidence of separation at the bond before the steel actually fractured, and after fracture a penknife could be inserted beneath the silver coating. Comparison of the results for samples 5 and 6 of Table 9 (p. 266) indicates that heating such specimens in an oxidizing atmosphere is more favorable to a good bond than heating in a non-oxidizing atmosphere. This statement is not a recommendation for the method, as the use of the nickel strike is simpler and assures perfect bonding. Further information on the adherence of these coatings appeared in the discussion on rolling electroplated steel.

(4) *Technique Adopted for Assembling Silver-lined Barrels.*—It was decided that in the manufacture of silver-lined containers that require brazing, a nickel strike should be used over the copper undercoat, and that induction heating should be used to permit extremely rapid application and localization of the heat, and accurate control of the temperature. Numerous tests have demonstrated that this technique is satisfactory. The generous application of brazing flux over the portion of the work exposed to high temperature was found helpful in minimizing the danger of blisters caused by oxygen penetration.

## 5. Silver Plating at Very High Current Density

### (a) Nature of the Problem

One phase of the silver-plating research work has been the development of a method of producing relatively low-cost silver-lined cans. For this purpose seamless drawn shells were provided by a cooperating company. These cylindrical shells form the body of the can, to which the top and bottom ends are subsequently attached. The ends can be blanked out of silver-plated sheet, but the can bodies or cylinders will have to be plated as such, since the silver lining is to be as thin as practicable, and certainly too thin to permit drawing the shell from plated circles. The steel used in making these can shells is very similar to the bright finish steel discussed earlier. It was found that with this steel, pore-free deposits of copper 0.0005 inch (0.0127 mm) thick could be obtained, upon which 0.00001 inch (0.00025 mm) of silver could be plated without any pores that extended to the copper. However, it was decided to experiment with the cans having a copper coating of 0.001 inch (0.025 mm) followed by 0.0001 inch (0.0025 mm) of silver, which were found to be pore-free by both laboratory and packaging tests. For the process to become commercial, a method would have to be found for plating the can shells on automatic machinery. To get production rates comparable with those now common in the manufacture of cans it would be necessary to use high rates of deposition. Attention was, therefore, directed to methods for reducing the time required to deposit copper and silver coatings of a given thickness on these cylinders.

It seemed that the most likely approach to the problem would be a

method of agitation that would reduce both anode and cathode polarization and permit silver or copper to be deposited at much higher current densities than are used in ordinary tank plating. Deposition of zinc at very high current density under somewhat analogous conditions has now been in commercial practice for some time. Wood<sup>16</sup> has discussed the function of agitation in the production of deposits of high current density. Mesle<sup>17</sup> has mentioned the plating of silver at 200 amperes per square foot current density.

### (b) Apparatus and Procedure Used in Tests

The essential feature of the apparatus, illustrated by Figure 5, is the use of a rapid and constant flow of plating solution past the cathode surface. Circulation is obtained by means of a water-circulating pump, driven at 1725 R.P.M. by a  $\frac{1}{4}$  horsepower motor. The plating chamber consists of a vertical iron pipe. This pipe is directly connected at its lower end to the discharge side of the pump. The plating chamber is surrounded by an outer jacket, which is connected at its lower end with the inlet side of the pump. The outer jacket has a removable lid which allows insertion of the work to be plated and forms a closed system when the pump is in operation. The outer jacket serves as a reservoir and takes care of the overflow from the plating chamber. The estimated pumping capacity of the pump is about 25 gallons (100 liters) per minute, and the apparatus and pump hold a total of about 1 gallon (3.5 liters) of plating solution.

The plating chamber contains a removable Bakelite tube. This tube carries contacts for the cathode and a central iron anode insulated from the cathode circuit. The sheet to be plated is bent to conform to the curvature of the tube and inserted within the tube.

The removable Bakelite tube, containing the steel cathode, was put through the following cycle before introducing it into the apparatus:

- (1) Vapor degreasing
- (2) Cathode cleaning (solution 1)
- (3) Acid pickle (solution 2)
- (4) 20 seconds in the copper-plating bath (solution 4) at a current density of 23 amp/ft<sup>2</sup> (2.5 amp/dm<sup>2</sup>) and a temperature of 60 °C.
- (5) 10 seconds in the silver strike bath (solution 6).

The work was thoroughly rinsed after each operation and after step (5) the anode was connected to its proper lead and the Bakelite tube placed in the plating apparatus. The pump and plating were started simultaneously.

### (c) Preliminary Results

Table 11 summarizes some results obtained in this apparatus. They indicate that it is possible, with the method described, to deposit silver satisfactorily at current densities of over 150 amp/ft<sup>2</sup> (16 amp/dm<sup>2</sup>).

Table 11.—Data on High Current Density Plating.

Specimen No.	Cell Voltage	Amp. per sq. ft.	Amp. per sq. dm.	Time (min.)	Average Thickness (Calc.)	Average Thickness from Wt.	Thickness Range Determined by Magne-Gage	Cathode Efficiency (%)	Pores per dm <sup>2</sup>	Composition*	Character of Deposit
1	5.5	52	5.6	1	0.00014				**	a	g
2	5.3	82	8.8	1	0.00022	0.00014	0.00010–.00020	64	16	a	h
3	6.0	114	12.3	1	0.00030	0.00014	0.00008–.00025	47	35	a	i
5	5.0	84	9.0	1	0.00022	0.00010	0.00007–.00012	45	4	b	i
6	5.8	153	16.5	1	—	—	—	—	**	b	j
7	5.8	163	17.5	1	—	—	—	—	**	b	j
8	5.7	89	9.7	1	0.00024	0.00015	0.00014–.00018	62	**	b	i
9	7.5	128	13.9	1	0.00034	0.00019	0.00019–.00021	56	**	c	i
10	7.7	95.6	10.4	1	0.00026	0.00012	0.00007–.00020	46	**	d	k
11	7.5	115	12.5	1	0.00031	0.00019	0.00017–.00024	61	**	d	k
12	7.3	165	17.9	1	0.00044	0.00024	0.00023–.00030	66	500	e	l
14	5.4	89	9.6	1.5	0.00036	0.00027	0.00024–.00030	75	500	e	i
15	7.5	166	17.8	5	0.00220	0.00156	—	71	160	f	m

\*Composition of Bath

	Ag (g./l.)	Free KCN (g./l.)	K <sub>2</sub> CO <sub>3</sub> (g./l.)
a	18.9	40.5	13.8
b	18.9	38.2	13.8
c	18.1	40.0	13.8
d	47.7	22.5	13.8
e	47.7	43.0	13.8
f	48.6	42.3	13.8

g Too rough to measure thickness. This run was made with the pump not running to determine maximum current density in a still bath.

h Fairly smooth and adherent.

i Smooth and adherent.

j Burnt appearance, non-adherent, too rough to measure thickness.

k Very smooth and shiny, adherent.

l Smooth, but no longer shiny; adherent.

m Adherent, too rough to measure thickness.

\*\* Too porous to count spots produced by ferroxyl gel.

Note: Specimens number 4 and 13 were used for exploratory tests.

## 6. Embrittlement of Steel in Plating

### (a) General

In the electroplating of can bodies of seamless drawn steel, it was sometimes observed that these plated steel cylinders were so brittle as to crack upon slight additional deformation. This indicated that hydrogen embrittlement had occurred and prompted an investigation of the embrittlement induced during plating.

It has long been recognized that, in the pickling of steel, hydrogen is absorbed which changes the physical properties of the steel, particularly its ductility. Except for stressed parts, such as springs, little attention has been given to the detrimental effect of plating upon ductility. Bablik<sup>18</sup> found that hydrogen absorption depends not only on the temperature and type of acid, but also on the kind of steel. Fuller<sup>19</sup> showed that the velocity of hydrogen penetration into iron is greater for specimens immersed in 1-per cent sulfuric acid than for specimens electrolyzed as cathode in that solution. The rate for electrolyzed specimens is proportional to the current and depends on the condition of the steel prior

to the pickling operation. Fuller also studied<sup>20</sup> the brittleness produced in steel springs by pickling in sulfuric acid and plating in a copper bath. Langdon and Grossman<sup>21</sup> studied the embrittling effects of cleaning and pickling upon carbon steels.

### (b) Procedure Used in Embrittlement Study

Two sets of specimens of bright finish steel, having 81 Vickers hardness, were employed. Two additional sets of specimens were prepared from heavier-gauge pieces of the same lot of steel, that was cold-reduced about 50 per cent in thickness to the same final gauge (0.009 inch or 0.023 mm) as the sheet used for the first two sets of specimens. The cold-reduced steel had a Vickers hardness of 184. Some specimens of both groups were subjected to treatment in only one of the following baths: cathodic alkaline cleaner (solution 1), acid pickle (solution 2), copper bath (solution 4), silver strike (solution 6), silver plating bath (solution 8). The other specimens were subjected in sequence to the operations in the cycle up to a given point. The change in ductility was measured by comparing the Erichsen test values of the specimens. In an effort to remove embrittlement, the specimens were heated for from 1 to 4 hours at temperatures from 68 to 752 °F (20 to 400 °C).

Table 12.—Effect of Specified Cleaning and Plating Operations on Ductility of Steel.

Plating Operation	Time (min.)	Bath Temp. (°C)	—Soft-Temper Steel—		—Hard-Temper Steel—	
			Erichsen Value (mm)	% Loss of Ductility	Erichsen Value (mm)	% Loss of Ductility
Control	—	—	9.5	—	5.0	—
Alkaline cleaner	2	100	9.3	2	5.1	0
Acid pickle	2	22	8.1	15	3.4	32
Copper plate	60	60	7.3	23	4.4	12
Silver strike	$\frac{1}{2}$	22	9.2	3	4.2	16
Silver plate	60	22	8.9	6	3.8	24
Anodic pickle	2	22	8.9	6	4.3	14
Nickel strike	10	—	9.5	0	4.0	20

### (c) Results of Embrittlement Tests

(1) *Effect of Individual Treatments.*—Table 12 gives the Erichsen values obtained on specimens subjected to a single operation in the plating cycle and tested promptly after the plating operation. The percentage loss of ductility was obtained by comparing the Erichsen values of these specimens with those of the untreated steel. On the soft-temper steel, acid pickling and copper plating most noticeably reduced the ductility. As much as 23 per cent loss occurred in the copper-plating operation, although even then this steel was fairly ductile. As this copper bath operates at only 60 per cent cathode efficiency, considerable amounts of hydrogen are liberated. The long exposure to nascent hydrogen in this bath is conducive to embrittlement. Hydrogen is also liberated by chemical action in the acid pickling bath.

The initial ductility of the hard-rolled steel is much lower, and hence

a reduction of, say, 25 per cent in ductility is far more serious than a similar reduction of initially highly ductile material. The more highly stressed steel may also be subject to caustic embrittlement by alkaline solutions,<sup>22</sup> as well as by hydrogen embrittlement. The data show that all the operations except the brief alkaline cleaning treatment produced some embrittlement. A loss in ductility of 32 per cent was produced by treatment of hard-rolled material in the acid pickling bath. The Erichsen value of the material after pickling in acid was only 3.4, and is indicative of material of very poor ductility.

(2) *Effect of the Sequence of Operations in the Plating Cycle.*—Table 13 shows that the reductions in ductility produced by separate treatments, such as pickling in acid, plating in the Rochelle salt copper bath, and applying the silver strike coatings, are not cumulative in their effects. Even if the acid pickling is omitted, the loss in ductility produced during copper plating is apt to result in a brittle steel. Apparently the steel becomes saturated with hydrogen and subsequent operations in the plating cycle cause little further reduction in ductility.

Table 13.—Effect of Sequence of Cleaning and Plating Operations on Ductility of Steel.

Series of Operations Including	Time (min.)	Bath Temp. (°C)	Soft-Temper Steel—		Hard-Temper Steel—	
			Erichsen Value (mm)	% Loss of Ductility	Erichsen Value (mm)	% Loss of Ductility
Control	—	—	9.5	—	5.0	—
Alkaline cleaner	2	100	9.3	2	5.1	0
Acid pickle	2	22	8.7	8	3.8	24
Copper plate	60	60	7.6	20	4.2	16
Silver strike	1	22	7.5	21	4.8	4
Silver plate	60	22	6.8	28	4.6	8

On the seamless drawn steel cylinders, Erichsen values of 2.4, 2.2, and 2.4 were obtained after the copper plate, silver strike, and silver plate, respectively, in the continuous plating cycle; whereas a value of 2.3 was obtained on a specimen treated only in the copper bath, 4.0 on a specimen only in the strike bath, and 3.9 on a specimen only in the silver bath. (The Erichsen value of the untreated steel was 5.1.)

(3) *Effect of Heating After Plating.*—The experiments on heating after plating to reduce embrittlement led to unexpected results. A loss in ductility resulted upon heating this steel either before or after treatment. For example, an untreated specimen heated for 2½ hours at 212 °F (100 °C) showed a loss in ductility of 19 per cent, and of 21 per cent after heating for 1 hour at 752 °F (400 °C). This same effect was observed on specimens heated after various operations in the plating cycle. For example, a specimen with a loss in ductility of 23 per cent after copper plating, increased in brittleness to give a loss of 32 per cent after heating for 1 hour at 212 °F (100 °C). Even after heating for 4 hours at 212 °F (100 °C) the low ductility persisted.

It is known that certain grades of low-carbon steel, similar to that under investigation, are subject to embrittlement on heating to tempera-

tures of 390 to 650 °F (200 to 350 °C). Van Wert<sup>23</sup> states that such brittleness is the result of iron oxide, carbide, or nitride being rejected from the alpha solid solution in such a manner as to reduce the ductility of the steel. This phenomenon is sometimes called "blue brittleness."

As the bright-finish steel used in these studies is subject to such heat embrittlement, the usual procedure for removing the embrittlement caused by hydrogen, *i.e.*, by heating the steel to a moderately elevated temperature, cannot be applied without danger of producing a still lower ductility. In fact, the embrittlement on heating the steel at 212 °F (100 °C) for 1 to 2½ hours is about as serious as that produced by hydrogen in the copper-plating bath. From the work of Langdon and Grossman<sup>21</sup> it would appear that this heating would largely remove the hydrogen and overcome the embrittlement which the hydrogen produced. That it did not improve the ductility indicates that "blue brittleness" more than counterbalances the effect of the higher temperature in removing hydrogen. As a result of this study, it was concluded that material of this type should be fully annealed to a soft temper before plating, if the reduction in ductility occurring in plating is too much for practical purposes.

## 7. Electroforming

### (a) General

Electroforming is inherently an inexpensive method for reproducing formed objects in metal by electrodeposition methods. It requires that a pattern of the object to be reproduced be used as a cathode in an electrolytic bath and, further, that this pattern have a surface which is electrically conducting. If the object is of complicated shape, the pattern must be fusible at a low temperature, so that the application of heat to the plated pattern will melt out the pattern.

Electroforming has been practiced over a period of many years, being applied to the reproduction in metal of statuettes, leaves, flowers, and other delicate objects. In such instances, the specimen to be reproduced in metal is coated with wax, which in turn is dusted with graphite or copper powder to make the surface conducting. This pattern is then plated as cathode in the usual fashion. Industrially the method of making electrotypes from wax plates is in common use. It is also possible to use as a pattern one made from a fusible alloy, which, being metallic, is not only conducting, but also has mechanical advantages over the wax plate.

Several plants are in operation in this country producing decorative objects, such as bookends and statuettes, using plaster patterns upon which a heavy coating of copper and nickel is deposited. In such cases, the plaster, of course, remains in place. The metal exterior gives mechanical strength and can be burnished, colored, or plated with chromium, silver, gold, or any other metal, in the usual fashion. There has also been a recent revival of electroforming in the electroplating of iron on patterns or "models" to form production molds for die castings, plastics and embossing dies. The iron deposit may be hardened by carburizing.

Recognizing the fact that silver finds considerable use in the chemical industry and that it might be more extensively used, particularly for small-scale and laboratory work, if apparatus possessing the corrosion resistance of silver were available at a low cost, it was decided that the Project would carry out some experiments in electroforming.

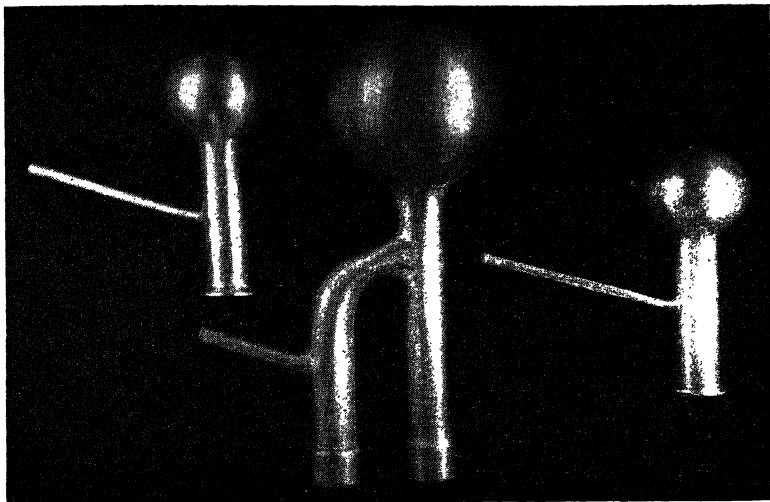


FIGURE 8. Electroformed silver distilling flasks.

#### (b) Procedure Used and Results

Figure 8 shows small distilling flasks electroformed by depositing 0.015 inch (0.37 mm) of silver upon a fusible alloy pattern, which was subsequently melted out to leave the hollow flask. In this case, the pattern was made by pouring the molten alloy into a glass flask and then breaking the flask away from the solidified metal pattern. A better method, but more elaborate, would have been to prepare a plaster cast of the flask and pour the fusible alloy into the plaster cast. In the first instance, the inside dimensions of the flask are reproduced faithfully, and in the second the outside dimensions.

A few comments regarding the procedure to be used if this method is adopted will now be presented.

An alloy containing 55.5 per cent bismuth with 44.5 per cent lead, known commercially as Cerrobased Alloy,\* is suitable for this purpose. The alloy melts at 255 °F (124 °C) and expands slightly on solidifying, so that it reproduces the details of the mold with accuracy. It can be

\* Cerrobased Alloy is sold by the Cerro de Pasco Copper Corp., 40 Wall Street, New York City.



removed from the electroformed vessel by heating in an oil bath to a temperature slightly above the melting point of the alloy. The pattern was given a silver strike and plated in a cyanide silver bath in the usual manner. It is advisable, however, to use a low current density and sufficient agitation to insure uniformity of the deposit and avoid roughness of the deposit. The anodes must be properly placed with respect to the parts of the pattern being plated, so that the wall thickness will be relatively uniform. Upon melting the lead-bismuth alloy, it may be found that the inside walls of the silver vessel are contaminated by the alloy. This contamination can be minimized by avoiding overheating, or preferably by applying a thin coating of iron or nickel before beginning to deposit silver. Subsequently, the iron or nickel can be dissolved out, using hot dilute hydrochloric or sulfuric acid, assisted by anodic action if necessary. In the absence of the iron or nickel layer, it has been found that a mixture composed of 25 per cent hydrochloric acid, 2 per cent nitric acid and 2 per cent sulfuric acid (by volume) is effective in removing the contaminated lead-bismuth layer with very little attack on the silver.

To avoid cracking the electroformed vessel as a result of a gradual expansion of the lead-bismuth alloy, the pattern should be aged at least 24 hours and then heated for one to two hours in boiling water. The pattern should also be melted out reasonably soon after plating has been completed. As buffing and polishing may produce enough heat to liquefy the alloy and crack the shell by the expansion of the liquid, such operations should not be undertaken while the fusible alloy pattern is still in place, unless great care is taken to avoid local heating. The fusible alloy may be used repeatedly.

## 8. Conclusions on Silver Plating for Industrial Purposes

### (a) Conclusions Based on Research at National Bureau of Standards

(1) Deep-drawing steel of a good commercial grade can be electroplated upon a copper undercoat with a pore-free silver coating 0.0001 inch thick.

(2) Deep-drawing steel of commercial grade can be electroplated upon a suitable undercoat with a pore-free silver coating as thin as 0.001 inch, and then subjected to drastic forming and heating operations without damage to the coating.

(3) A copper undercoat at least 0.001 inch thick is recommended. For those forming operations in which heating is involved, the copper undercoat should be separated from the silver deposit by a nickel deposit, or else the steel should be given a nickel strike coating, for example, from Wood's nickel bath, before depositing the silver coating.

(4) Under certain conditions blistering and peeling of silver coatings may occur if the plated material is exposed to relatively high tempera-

tures in an oxidizing atmosphere. This is caused by diffusion of oxygen through the silver and the formation of oxide on the base metal. Whether oxidation actually occurs or not will depend on the temperature, the time at elevated temperature, the nature of the base metal, and the thickness of the silver coating.

(5) Silver-plated steel and objects fabricated from it, may be joined or assembled by the use of low-temperature silver brazing alloys and induction heating, without recourse to a protective atmosphere.

(6) The possibility of manufacturing relatively low-cost silver-lined containers, such as barrels, drums, and cans, has been demonstrated.

(7) It has been shown that deep-drawing steel may be electrolytically coated with silver and subjected to extensive reduction by cold-rolling, to annealing treatments, and further cold-rolling without separation or injury of the silver coating. The methods described are applicable to the production of silver-coated steel in large sheets.

(8) Embrittlement of steel may occur in both acid and alkaline plating baths, as well as in the strike and pickling baths. Such embrittlement may be serious if the steel has been work-hardened and has low initial ductility. Annealing of the work-hardened steel prior to plating is recommended.

(9) Smooth, adherent deposits of silver may be produced at a current density as high as 165 \* amperes per square foot (17.9 amp./dm<sup>2</sup>). The method described can be applied, at least under laboratory conditions, to the rapid deposition of silver for can linings.

(10) The production of thin pore-free deposits of silver requires:

(a) Selection of a base metal of relatively smooth surface, free from pits, scale, scratches, and excessive amounts of solid non-metallic inclusions. Alternatively, a pore-free electroplate (which may need to be of substantial thickness) of a suitable metal, such as copper, may be deposited on the base metal upon which a thin pore-free coating of silver may, in turn, be deposited.

(b) Scrupulous care in maintaining plating solutions substantially free from suspended matter.

If these two requirements are met, conventional plating procedure can be used to deposit (on a polished electrolytic copper surface) a silver coating 0.00001 inch (0.00025 mm) thick that is free from porosity.

### **(b) Conclusions Based on Work of Mathers and Gilbertson**

(1) Adherent, smooth deposits of silver 0.05 to 0.07 inch (1.3-1.8 mm) thick can be plated on properly cleaned and treated low-carbon steel by use of a copper or silver strike preceding the silver-plating operation.

(2) Such smooth, dense deposits are suitable for use in bearings and for lining industrial vessels.

\* In more recent experiments carried out at higher temperatures current densities as high as 200 amperes per square foot have been used successfully.

(3) The porosity of electrodeposited silver on steel is dependent on the thickness of the plate, the roughness of the base metal, and the method of applying the silver coating.

### III. RESEARCH ON DEPOSITION OF SILVER ALLOYS

#### (a) General

The electrolytic deposition of alloys is used commercially where an alloy deposit has desirable properties and a relatively thin coating of the alloy is all that is needed. Brass-plated steel hardware may be cited as an example. Sometimes the normal method of producing alloys is either not applicable or is less suitable. This appears to be the case for silver-lead alloys to be used for bearings, and is discussed in Chapter 8. As in the case of alloys produced by thermal methods, electrodeposited alloys have properties which frequently are superior to those of the component pure metals. In the case of silver alloys, it seems reasonable to suppose that it might be possible to electrodeposit a silver alloy, which would be harder than pure silver, and yet possess a desirable resistance to corrosion. Also, more wear-resistant or tarnish-resistant silver alloys which still retain good electrical conductivity would be desirable for electrical contacts. Similarly, where silver is used as a corrosion-resistant lining for chemical equipment, the softness of the metal is sometimes a handicap and greater hardness without loss of corrosion-resistance would be welcome.

Such instances prompted the sponsorship of a fellowship at Indiana University to study the electrodeposition of silver alloys. This work was undertaken by Aaron D. Johnson under the supervision of Dr. F. C. Mathers, and is reported in detail in the paper, "The Electrodeposition of Silver Alloys from Aqueous Solutions" by Frank C. Mathers and Aaron D. Johnson, [*Trans. Electrochem. Soc.*, **74**, 229 (1938)].

In the bibliography will be found numerous references on the electrodeposition of alloys of silver with cadmium. Other references relate to the deposition of silver with copper, cobalt, nickel, zinc, tin, gold, platinum, aluminum and other metals. Mathers and Johnson<sup>24</sup> obtained electrodeposits of silver with nickel, cobalt, cadmium, copper, iron, zinc, and lead. The baths used were composed of solutions of complex salts selected because of the proximity in them of the decomposition potentials of the various metals to that of silver.

A summary of the results obtained shows that further exploration of this field will probably be very fruitful. Because this work was of a survey nature, it was impossible under the circumstances to fix the conditions required to produce a deposit of given composition, and in the paper by Mathers and Johnson it will be noted that in many instances the composition of the deposit varied widely with no indication of what operating conditions were responsible for the change. As the work progressed it was realized that the voltage was probably a controlling

factor, but little data relating to this were obtained in the earlier experiments. Nevertheless, the fact that the deposit showed the presence of the second metal indicates the feasibility of this method for producing the silver alloys reported; and it is particularly worthy of note that harder silver deposits were obtained with a small amount of nickel, and that the electrodeposited silver-zinc alloy was more tarnish-resistant than pure silver, which is in accord with the data of Jordan, Grenell and Herschman.<sup>25</sup> Another feature of interest was the observation of Mathers and Gilbertson that silver deposits containing a fractional percentage of iron, although not tarnish-proof, were noticeably more resistant to tarnish than any of the other alloys studied, and they also apparently exhibited a greater resistance to acids.

### (b) Results

*Copper-silver alloys.* 1. Copper and silver were codeposited from their complex thiourea solutions. The alloys ranged in composition from 2.0 to 63.6 per cent copper.

2. The alloys were not brittle, and were finely crystalline and soft.

3. Increasing the percentage of copper in the alloy decreased the resistance of the silver to tarnish.

*Nickel-silver alloys.* 1. Nickel-silver alloys were deposited from thiocyanate and tartrate solutions. The deposits were outstanding for their hardness.

2. Deposits containing up to 74 per cent nickel were plated from thiocyanate solutions. These deposits were of good quality and were plated to an average thickness of 0.0028 in. (0.07 mm).

3. Excellent heavy, white deposits of nickel-silver alloys containing up to 0.6 per cent nickel were plated from tartrate solutions. The deposits were definitely harder than those of silver electroplated from cyanide solutions, but could not be plated directly upon copper or steel.

4. The deposits from the tartrate solutions were brittle.

5. Nickel-silver alloys tarnished more easily than did pure silver.

*Iron-silver alloys.* 1. Iron-silver alloys were deposited from thiocyanate and thiosulfate solutions.

2. The maximum percentage of iron that was deposited with the silver was 1.36 per cent. The deposits had an average iron content of 0.5 per cent.

3. The thiosulfate bath produced deposits that were smoother, more finely crystalline, and more adherent than did the thiocyanate bath.

4. The thiosulfate bath was more difficult to control than was the thiocyanate bath. The former had a tendency to "break down" at temperatures above 40 °C (104 °F), and current densities above 1.9 amp/ft<sup>2</sup> (0.2 amp/dm<sup>2</sup>) produced black spongy deposits.

5. Iron-silver alloys were more resistant to tarnish than any of the other silver alloys studied; yet they were not tarnish-proof.

6. Iron-silver alloys were considerably more resistant to acids than any of the other alloys produced.

*Cadmium-silver alloys.* 1. Cadmium-silver alloys were deposited from their thiocyanate and thiourea solutions.

2. Good codeposits of silver and cadmium, containing from 0.2 to 30.2 per cent cadmium, were plated from the thiocyanate solutions. The deposits from the thiourea solutions were of very poor quality, being more or less spongy.

3. The electrodeposited cadmium-silver alloys were not tarnish-proof; in fact, the addition of cadmium to the silver reduced the tarnishing only slightly.

*Zinc-silver alloys.* 1. Zinc-silver alloys containing up to 3.79 per cent zinc were deposited from silver-zinc ammonium nitrate solutions.

2. The concentration of zinc in the alloy was largely dependent upon the concentration of zinc in the bath. The greater the ratio of zinc to silver in the bath, the more zinc in the deposit.

3. Tartaric acid made the deposit much more dense but at the same time more brittle.

4. Zinc-silver alloys were slightly more resistant to tarnish than was pure silver.

*Cobalt-silver alloys.* 1. Much higher percentages of cobalt were alloyed with silver in the thiocyanate baths than in the thiourea solutions. Seventy-four per cent cobalt was codeposited with silver from the former baths, but such deposits were spongy. Only 0.57 per cent cobalt was codeposited with silver in the latter bath, but the deposits were smooth, finely crystalline, hard, and not brittle.

2. The thiocyanate bath from which silver and cobalt were deposited was unstable and irregular in the results obtained.

3. The presence of cobalt in the silver deposit noticeably increased the hardness of the deposit.

4. Cobalt-silver alloys tarnished with more ease than did silver itself.

*Lead-silver alloys.\** 1. Lead-silver deposits containing from a trace to 63 per cent lead were deposited from fluosilicate solutions. The deposits were powdery and thin. The cathode current efficiency was low.

2. Lead-silver deposits containing up to 0.5 per cent lead were deposited from nitrate-tartrate solutions. These deposits were white, smooth, hard, and finely crystalline. There was very little treeing or burring, and the deposits could be built up to at least 0.04 inch (1 mm) in thickness. The one objection, other than the low lead content, was the brittleness of the deposits.

3. Lead-silver deposits containing from a trace to 72 per cent lead were deposited from their potassium silver cyanide-potassium plumbite solutions. The color and hardness of the alloys depended upon the lead concentration of the alloy. The alloys could be deposited to 0.04 in. (1 mm) in thickness.

4. Silver-lead alloys tarnished more quickly than did silver itself.

\* Attention is invited to the discussion in Chapter 8 pertaining to the electro-deposition of lead-silver alloys for bearings.

# Chapter 11

## Chemical and Vaporized Coatings

By A. M. SETAPEN \*

There are a number of methods for producing a thin silver coating on glass or other material, and each one has its own special advantages and applications. This chapter deals with the chemical reduction and vaporization processes.

### THE CHEMICAL REDUCTION METHOD <sup>1, 2, 3, 4</sup>

In 1835 Liebig<sup>5</sup> made a scientific announcement of fundamental importance when he wrote that when aldehyde is mixed with silver oxide and water and then heated, the silver oxide at once becomes reduced and metallic silver is deposited on the side of the test tube in the form of a brilliant mirror. From the time of Liebig's first mirror, there has been process upon process given in the literature for silvering by the chemical reduction method. All of these are slight variations or modifications of Liebig's method (consisting usually in some variation of the reducing agent employed to precipitate the silver) and most of them can be regarded as being mere recipes.

It is felt today, over a century after Liebig's first mirror, that the method of silvering by chemical reduction is still an art, and not a scientific process. Different operators will attain different degrees of perfection of the silvered surface, but—and this is important—each will have a silvered surface. It is perfection which is the art.

There are a great many applications for which a thin silver film, although not absolutely perfect, is desired. It is for this reason that complete details of a few of the many formulas for chemically depositing silver are given. They are (1) the Brashear process, in which the silvering solution contains potassium hydroxide as well as ammonium hydroxide as the reducing agent, and, processes employing (2) Rochelle salt,<sup>†</sup> and (3) formaldehyde as reducing agents.

Although silvering is not usually considered a dangerous procedure, it is deemed wise to introduce the subject by a discussion of the precautions which should be taken in handling the solutions.<sup>6, 7</sup>

In all methods commonly used for chemical deposition, the silver is in an ammoniacal solution prepared by adding ammonium hydroxide to

\* Silver Research Associate, National Bureau of Standards.

† Potassium-sodium tartrate,  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ .

a solution of silver nitrate, and the silver is subsequently precipitated in the metallic form by the addition of a suitable reducing agent. In this solution compounds may be formed which are violently explosive and which detonate as a result of the slightest mechanical disturbance. At times these explosive compounds have formed, with serious consequences, during the process of silvering glass; and instances are recorded<sup>8,9</sup> in which explosions of this nature have resulted in loss of sight through the action of ammonia on the eyes, or have been sufficiently violent to produce considerable property damage. These explosions are more likely to occur when using a formula in which potassium hydroxide is one of the constituents of the silvering solution, as in Brashear's method. It seems, however, that they are possible occurrences with any of the methods for chemical silvering. The use of solutions of lower concentration greatly decreases the probability of explosions, and experience has shown that certain formulas, such as those given herein, do not produce explosive mixtures, if the stated precautions are taken. The explosion hazard is greatly increased if the residue remaining after silvering is allowed to become dry, or if empty vessels in which the silvering solution has been

Table 1.—Composition of Solutions for Use in Chemical Reduction Method.

	Brashear		The Reducing Solution		Formaldehyde	
	Metric Units	English Units (ounces)	Metric Units	English Units (ounces)	Metric Units (ml)	English Units (ounces)
Tablet or Granulated Sugar	90 gm	3.17				
Nitric Acid	4 ml	0.14				
Silver Nitrate			2 gm	0.07		
Rochelle Salt			1.7 gm	0.06		
Formaldehyde					40 l	1.35
Distilled Water	1 l	33.81	1 l	33.81	200 l	6.76
	Brashear		The Silvering Solution		Formaldehyde	
	Metric Units	English Units (ounces)	Metric Units	English Units (ounces)	Metric Units	English Units (ounces)
A						
Silver Nitrate	20 gm	0.71	10 gm	0.35	20 gm	0.71
Potassium Hydroxide	10 gm	0.35				
Distilled Water	400 ml	13.52	100 ml	3.38	1 l	33.81
B						
Silver Nitrate	2 gm	0.07	3 gm	0.10	2 gm	0.07
Distilled Water	30 ml	1.01	30 ml	1.01	100 ml	3.38

All the chemicals used in the preparation of the solutions must be of high purity; the grade known to the trade as C.P. will be found satisfactory.<sup>13</sup>

\*Dilute to one liter after the addition of ammonium hydroxide.

prepared or stored are allowed to dry without first having been carefully cleaned. Consequently, all vessels containing silvering solutions should be carefully cleaned immediately after use, and all residues remaining from the silvering should be washed down the sink or otherwise safely disposed of without delay. When silvering is done regularly and on a

large scale, it becomes advisable to save all residues for the recovery of the silver. In such cases, sufficient hydrochloric acid should be added to all spent solutions and residues to acidify them. This precipitates the silver and also removes all danger of explosion. It is further recommended that the silvering solution for the Brashear process should not be stored, but prepared only as required.

The Brashear<sup>10, 11, 12</sup> formula is probably the most generally used process for silvering surfaces when a thick, adherent deposit of silver is required and the reflection is from the front surface. Table 1<sup>3</sup> gives the composition of the solutions used in this formula, as well as those used in the Rochelle salt and formaldehyde formulas.

The reducing solution for the Brashear process is boiled for five minutes and allowed to cool before use. It is preferably prepared in large quantities as it does not deteriorate, and is said to improve with age. If it is to be stored, 175 ml of grain alcohol is added to the cool solution in the quantity given in Table 1, as a preservative. Boiling may be omitted if the reducing solution is prepared one or two weeks in advance of the time of use.

In preparing the Rochelle salt formula, the reducing solution of silver nitrate in distilled water is heated to the boiling temperature and the Rochelle salt added, after which it is stirred while boiling for five minutes. It is then filtered before cooling and stored in a dark bottle.

In preparing the silvering solution, aqueous ammonia is added to the silver-nitrate solution in quantity just sufficient to redissolve the precipitate first formed. An operation of this sort, which is characteristic of each of the formulas given, is the most important step in the preparation of the solution. A relatively small excess of ammonia prevents any deposition of silver, whereas a deficiency in ammonia results in an excess of precipitated silver oxide which is undesirable and must be removed by filtering. To insure the addition of the correct amount of ammonia, the following procedure is recommended. Solutions A and B, (Table 1) are prepared in accordance with the formula to be used. The ammonia, which should be C.P. and concentrated (specific gravity 0.99 to 0.90), is added to solution A in small portions, and after each addition the solution is well shaken. At first the amount of precipitate formed will increase greatly with each addition of ammonia. The successive processes of adding ammonia and shaking the solution thoroughly are continued until the precipitate begins to redissolve, and further addition of ammonia tends to clear the solution. As the solution becomes clear, the ammonia should be added more cautiously and the duration of the intermediate period of shaking increased, in order to give each portion of ammonia full opportunity to redissolve the precipitate as completely as possible before another addition of ammonia is made. It is desirable to add the minimum amount of ammonia that will redissolve the precipitate initially formed, but it is better to finish with a solution in which there is a slight excess of silver rather than an excess of ammonia.



Accordingly, after one has added to solution A what is judged to be the requisite amount of ammonia, solution B is added in small amounts by following the procedure that was used in adding ammonia. If the correct amount of ammonia has been added to solution A, the addition of a small amount of solution B will result in a darkening of the solution caused by the precipitation of silver oxide, which will be permanent and will not disappear even if the solution is shaken thoroughly and allowed to stand for an hour or two. If, however, ammonia has been added in excess, the precipitated silver oxide will redissolve and the solution will clear. In this case one must continue to add solution B until the permanent darkening of the solution is secured. *No attempt should be made to use a silvering solution until this darkening has been obtained*, even if it should be necessary to prepare an additional amount of solution B. If this procedure is followed, a slight excess of silver is assured and the silvering solution is certainly in a condition to be reduced readily when used. The precise method, described above, of determining the amount of ammonia to be added to the silver-nitrate solution is the procedure recommended when silvering is done at infrequent intervals, because in such cases there usually exists an uncertainty regarding the exact strength of the aqueous ammonia solution which is used. If, however, much silvering is being done and the solutions are prepared in large quantities, the amount of ammonia to be added can probably be satisfactorily controlled by measurements of density and volume, and the delay incident to the titration process can be avoided.

In using the Brashear formula, the solution applied to the surface to be silvered is made by mixing one part by volume of the reducing solution with four parts of silver-nitrate solution. Equal portions of the silver-nitrate and reducing solution are mixed, immediately before silvering, with the Rochelle salt formula. Silvering may be done at room temperature, although it will be found advantageous to have the surface to be silvered slightly warmer than the solution. When silvering with the formaldehyde formula, five parts of the silver-nitrate solution are mixed with one part of reducing solution immediately before application to the surface.

The prime essential for success in silvering is cleanliness of the surface to be silvered. This cannot be too strongly emphasized, because if it is neglected, failure will result, no matter how perfect the application and methods may be. The usually recommended degreasing and cleaning agents are to be employed for cleaning. The selection of the degreasing agent should be made with care when silvering an organic plastic material, as the degreaser may attack it. A new, fresh surface, free from fingerprints will, in most cases, silver better than an old surface which has been exposed to the atmosphere for a relatively long period of time.

In commercial silvering, many manipulators follow the cleansing by a vigorous swabbing with a saturated solution of stannous chloride

( $\text{SnCl}_2$ ) which is carefully rinsed off with warm water. The stannous chloride tends to make the surface wet more easily, and it may be that certain forms of "soapless soaps" will serve equally well for this purpose. The application of stannous chloride favors the production of a heavy deposit under conditions which otherwise would yield only a thin, unsatisfactory film.

Most of the instructions on silvering recommend that glass surfaces be wet immediately prior to the application of the solutions. On the other hand, experience has shown that when an organic plastic, such as vinyl resin, is silvered for front reflection,\* a thoroughly cleaned, dry surface is more suitable.

### Relative Merit of Different Formulas for Silvering

Of the formulas which have been given, the Brashear and Rochelle salt processes are, perhaps, the most generally employed and are regularly used for the production of mirrors. For reflecting telescopes and other applications, where reflection from the front surface is required, the Brashear formula is commonly recommended for obtaining a film of silver which is relatively very thick, has a very high coefficient of reflection, and adheres firmly to the glass, thus permitting frequent polishing. However, equally thick coats, which withstand polish well and which are satisfactory for front reflection, can be obtained with the Rochelle salt formula.

James French<sup>4</sup> reports that a surface silvered by the Brashear process reflects 98 per cent of the incident light, while a similar surface silvered by the Rochelle salt process reflects about 92 per cent.

If the silvering is done properly by any of the methods, if care is taken in cleaning and if pure chemicals are employed, a bright silvered surface will be obtained. However, as stated previously, improper cleaning will yield inferior results and a brown, stained surface. Brown stains are also attributable to impurity of the chemicals.

Pinholes, or pores in the silver, may result from evolution of gas, but are more commonly caused by the presence of dirt, dust or protuberances on the surface. The precipitate which forms during the course of the reaction sometimes gives rise to porosity also by settling out on the surface in the form of a bloom. It is very difficult to obtain a pore-free silver coating on a surface of any large size when dealing with these extremely thin films.

The thickness of a silver film may vary from  $1.2 \times 10^{-6}$  inches, ( $30 \times 10^{-6}$  mm) for a very thin film to approximately  $7.9 \times 10^{-6}$  inches, ( $200 \times 10^{-6}$  mm) for a very thick film. It is advisable to make more than one application of the silvering solutions when an extremely thick coat is desired. This, however, usually results in a dull front-reflecting

\* An example of a back reflecting surface is the ordinary household mirror. Reflection of the silvered surface is through the glass.

surface. A heavier deposit is obtained if the solutions are allowed to remain in contact with the surface a long time, but there is a limit to this because, as the reaction goes on, a heavy brown precipitate forms which no longer deposits as a bright silver film. Heating of both the solutions and the surface to be silvered speeds up the reaction and results in a rather thick deposit. It might be said that there is an inverse relation between the thickness and quality of the deposit (the thicker the deposit, the lower the quality) unless careful, accurate control is maintained.

Chemical silvering is usually done on glass, but more recently this method has been employed for the silvering of various plastic and metallic materials. The American Silver Producers' Research Project,<sup>14</sup> in an endeavor to find a suitable method for obtaining a silver-lined container, carried on a research program of silvering various types of plastics. The following table gives the results of these experiments:

Materials Silvered by the Brashear Chemical Reduction Method

Plastics	Character of Deposit	Remarks
Casein	Good	Sample pigmented
Cast phenolics	Excellent	Adherent (sample pigmented)
Cellulose nitrate	Good	No staining of undersurface
Ethyl cellulose	Poor	Staining of undersurface
Cellulose acetate	Good	Staining of undersurface
Methacrylate resin	Fair	No staining of undersurface
Styrene resin	Poor	Staining of undersurface
Vinyl resin	Excellent	Adherent, no staining
Metals	Character of Deposit	Remarks
Steel	Good	(Bright finish, deep drawing)
Tin (Tinplate)	Good	Adherent deposit

The chemical reduction method of silvering is most widely used in the making of mirrors, and also finds application in the manufacture of silvered electric-light bulbs and Thermos bottles. It is not easily adaptable to a rapid, large-scale production, as the reaction time is relatively long (1 to 20 minutes, depending on the solutions used). More recently conveyor-belt methods and spray processes<sup>15, 16, 17</sup> have been developed and these have speeded up production methods considerably. However, the reduction method has not been considered seriously for the lining of cans, for instance, chiefly for two reasons: (1) the vaporization method, as described later, appears to be better suited, and (2) the efficiency of the process is not very great and requires the working up of by-products. Its chief advantage is the fact that good coatings can be obtained with little experience and with a negligible investment in apparatus. Also, it is adaptable to silvering objects of irregular or complicated shape, such as Christmas-tree decorations and the inner wall of a Thermos flask. It is an economical method used in the manufacture of household and other types of mirrors.

## THE VAPORIZATION PROCESS 1, 3, 18, 19, 20

The vaporization method for depositing silver is, at the present time, being widely considered commercially. Although the process has not been commercialized to a great extent, a great deal of important information concerning it is now rapidly being accumulated.

In many respects, the deposit obtained by vaporization is similar to that obtained by chemical reduction. The important difference to be remembered when comparing the two processes is the fact that vaporization is a science and, as mentioned previously, chemical reduction is still considered an art. The quality of the film produced by vaporization does not depend on the technique of the operator and different operators can therefore obtain the same degree of perfection of the deposit when using the vaporization process. Close control of the thickness is possible and there is no recovery problem with which to deal. The "bloom" which is usually present on the surface of a chemically deposited film is not formed by the vaporization method. This becomes very important when a front-reflecting surface is desired, as in the case of telescopic mirrors, containers, and certain decorative materials.

A description of the vaporization process follows, but those interested in details of the method are referred to the bibliography for sources giving more complete information.

The vaporization process, briefly stated, is the distillation of a metal or non-metal from a filament or other source of heat in a vacuum chamber under reduced pressure of about  $10^{-2}$  mm of mercury or less. When the vapor pressure of the metal, which is governed by temperature, equals or exceeds the pressure of the chamber, the metal truly boils, and molecules of the metal distill off in all directions and deposit on the nearby cooler surfaces in the form of a thin film. The degree of vacuum required for successfully carrying out the process is such that the mean free path (the average distance a molecule travels before collision) of the molecules is longer than the distance between the metal source and the work to be coated. This then permits the metal to travel in all directions from its source to the object without loss of energy. The relatively high initial energy of the molecules is maintained if only a minimum number of collisions take place. It seems likely that this would favor greater adherence of the deposit, although the author knows of no experimental evidence verifying this assumption.

The equipment and apparatus required to operate the vaporization process has many variations. For instance, the vacuum can be obtained by the use of any one or combinations of the vacuum pumps now available, such as mercury vapor, oil diffusion and mechanical pumps of various types. The character and amount of work usually determine the pumping system to be employed.

The speed with which the metal vaporizes at a given pressure is controlled by the heat supplied to the metal. It can be seen that, in

order to fulfil the requirements, the heat source should be capable of maintaining an elevated temperature for the duration of the vaporization and should reach this temperature very rapidly. The heat source itself should be of small heat-absorbing capacity, so that when the power is cut off cooling is prompt, and the work to be silvered is not subjected to any unnecessary heating by radiation from a glowing filament or crucible.

A filament is usually employed for supplying the heat to the metal to be vaporized, and also acts as a support for it. High-frequency current for heating has been considered in experiments conducted by the American Silver Producers' Research Project.<sup>21</sup> A small furnace consisting of a coil having a few turns of either tungsten or silver wire has proved satisfactory for the melting of pellets of silver the size of a pea in less than one minute. The method of heating is described in U. S. Patent No. 2,164,332, which deals with an apparatus for applying mirror surfaces to the interior of lamp bulbs.

The size and number of pieces of the material to be coated at one time govern the size of the vacuum chamber, which in turn determines the type of pump to be used. A large telescope mirror, for instance, requires a large chamber, which may be two feet in diameter and at least two feet high; in order to obtain the desired vacuum, diffusion pumps must be employed. A long pumping time is necessary for out-gassing and bringing the chamber to the high vacuum required. Most materials, such as glass and metals, have a certain amount of absorbed moisture and gases on the surface, or within the material, and these are given off at the low pressures required for vaporizing. The removal of these is known as out-gassing of the system. For small work requiring chambers approximately 6 inches in diameter and 8 inches or less in height, it has been found that high-capacity mechanical pumps are available which can do the required pumping in a very short time. The extremely low pressure,  $10^{-5}$  mm of mercury and less, recommended for large work, is not necessary when small chambers and short distances between filament and object are involved. (It must be borne in mind that only recently has the vaporization process been commercialized for small work.) Thus the pumping time, which is quite appreciable with large chambers and therefore prohibits large-scale quantity production, becomes tolerable with small units.

If rapid exhaustion of the vacuum chamber is of prime importance, it must always be remembered that short, straight connections of large diameter are to be employed. *The flow of gases at these low pressures is governed by laws of diffusion rather than by laws of hydraulics.*

A convenient arrangement\* which has been used by the Silver Project in the experimental work for silver lining containers is shown in Figure 1. The silver to be evaporated is placed on the loops of a tungsten coil fila-

\* Similar equipment and apparatus are described in references 1, 3, 22, 23, 24.

ment (30-mil wire) which is centered inside of a can supported by a magnet, as shown. Filament location is very important as the uniformity of the thickness of the film depends on the relationship of the work and the filament. The thickness of the deposit varies inversely as the square of the distance between the work and the filament and is heaviest where

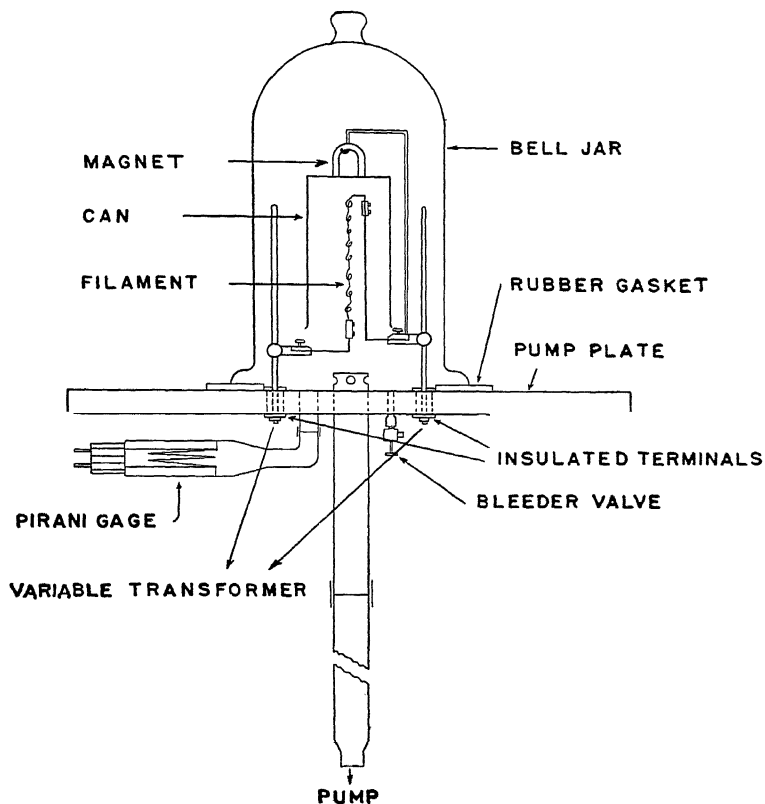


FIGURE 1. Laboratory apparatus for lining containers by evaporation.

the filament is closest to the specimen. It has been found advisable during the first heating, and only then, to wind the filament with both fine platinum and silver wires. The platinum aids in wetting the tungsten with silver.<sup>25</sup> Some experimenters claim that for evaporation of silver the filament should be made of molybdenum rather than tungsten, as the former metal is more easily wet with silver. Small loops are recommended in making up the filament, because in this way surface tension keeps the

molten silver globules from falling off. The electrical leads must be tightly sealed in the pump plate. Some systems have a third electrode for allowing the vacuum chamber containing the work to be filled with a glow discharge during the preliminary evacuation. This discharge effects the final cleaning of the surface, but is not necessary in all cases. The vapor pressure of all materials used in the assembly must be low enough to prevent the introduction of copious quantities of vapor. This requires careful selection of gasket material, sealing compounds, etc.

A Pirani gauge is used to measure the vacuum; this is preferred to the McLeod gauge when many, or instantaneous, readings are desired. There are, of course, many types of vacuum gauges that can be employed. It was found that bright, adherent silver could be deposited on glass, various organic coatings and plastics at a pressure of about 3 microns; and on a particular organic base used in one set of tests to note the effect of pressure, good deposits were obtained with pressures of 1 to 100 microns.

In the set-up shown in Figure 1, a mechanical pump having a free air capacity of 198 liters per minute and 85 liters per minute at 1 micron, was used and the desired vacuum ( $5 \times 10^{-3}$  mm of mercury) was obtained in about 1 minute. The heating of the filament by resistance was controlled with suitable transformers. To vaporize the silver, the filament was heated to incandescence for a second or more, depending on the thickness of deposit desired.

As in the chemical reduction process, cleanliness of the surface to be coated is important to obtain a good deposit. A chemically clean, or new surface, free from dirt, grease, or fingerprints, will usually give satisfactory results. To appreciate this fully, attention is called to the fact that moisture condenses very uniformly on a clean surface, whereas it collects in large patches on a greasy, unclean surface. The chemist determines the cleanness of glass by allowing water to run off the surface. If the water runs off uniformly the surface is considered clean, whereas if it runs off in streaks the surface is said to be dirty.

The appearance and character of the deposit depends a great deal on the surface to be coated. Obviously the material itself must have a very low vapor pressure. Adherent, bright, mirror-like deposits of silver are easily produced on glass. Vinyl resin also is a suitable base material on which silver may be deposited. There are a great many other materials, including plastics, enamels and metals, upon which adherent, vaporized deposits of silver can be produced. Cellulose acetate, cellulose nitrate, Cellophane, ethofoil, paper and other materials have been silvered satisfactorily.

#### PROPERTIES OF THE FILMS <sup>26-32</sup>

The silver film obtained by vaporization upon a suitably glossy surface is bright and adherent. Film thickness can be closely controlled and made either less than or greater than opacity, as the case may be.

(An opaque silver film is about  $3 \times 10^{-6}$  inch or  $76 \times 10^{-6}$  mm thick.) It is a very convenient method for making half-silvered mirrors. Properly deposited films have a very high reflectivity and figures up to 99 per cent reflection factor in the visible range are reported in the literature.<sup>33</sup> Large telescopic astronomical mirrors have been prepared with aluminum by the vaporization method. Aluminum is used in this particular application because it has a higher reflectivity for the short wave-lengths or ultraviolet light range than has silver, and, therefore, is especially suitable for reflecting the light of short wave-lengths emitted by the stars. Silver has a higher reflectivity than aluminum for radiation of longer wave-length, such as falls into the visible portions of the spectrum.

Claims are made that vaporized silver films are more tarnish-resistant<sup>23, 33</sup> than other forms of silver.

Goche and Wilman<sup>34</sup> studied by electron diffraction the structure of silver films prepared by vaporization on rock salt cleavages. Many other investigators have made similar studies, and many of these references are included in the bibliography of this book.

The silver films obtained by vaporization are by no means pore-free, and it is felt that this porosity is caused by minute projections, such as dirt or dust on the surface, or perhaps by contamination of the vaporized material. However, films produced by this method are as good as, or perhaps better, from the standpoint of porosity, than those of any other process when equal thicknesses are compared.

The character of the deposit obtained depends a great deal on the vacuum. If vaporization is done in an insufficient vacuum, a spongy, colored deposit ranging in color from black to pale yellow will result. In some experiments performed by the Silver Project, it was found that in silvering certain plastic materials, a rose- or purple-colored deposit was obtained. This was traced to the presence of grease on the surface. A. H. Pfund<sup>35</sup> describes the evaporation of bismuth from a tungsten spiral; at a pressure of  $10^{-4}$  mm of mercury the deposit was metallic and highly reflecting, but at 0.25 mm of mercury a black film was produced. For the production of very uniform and highly reflecting surfaces, it is recommended that the silver be evaporated quite rapidly.

The adherence of silver films on vinyl resin may be improved by heating the material after silvering for about 10 minutes at 100 °C. Films treated this way will withstand stripping by scotch tape. This simple method of testing for adherence is to attach a piece of "scotch cellulose tape" or other adhesive material to the surface of the deposit and then peel off the tape. An adherent deposit will not strip off.

Vacuum evaporation is much better adapted to large-scale quantity production than the chemical reduction process, and at the present time machines have been developed for continuous processes involving the vacuum technique.

An interesting example of production machinery developed for vacuum work is that used in vacuum packaging of such commodities as coffee.



Attention is also invited to the latest one-piece sealed-beam automobile headlight, the reflector of which has been coated by the vacuum evaporation process on machines operating continuously. A similar commercial application is the production of inside-silvered electric lamps. Still another illustration is radio tube manufacture, in which process the tubes are automatically evacuated and heat developed inside the tube by currents induced by high-frequency methods distills a film of magnesium, used as a "getter," onto the wall of the tube. Machines have been developed to silver-coat sizable objects by evaporation at the rate of hundreds an hour and at a very low unit cost. Small articles such as combs, buttons, pins, etc., are now being metallized on a production basis by means of the evaporation process.

It may be safely predicted that metallizing by the vacuum evaporation process will be applied much more widely as soon as the process and the utility and beauty of such coatings become generally known. Many applications of silver coatings produced by this method come to mind, and, aside from obvious decorative and ornamental possibilities, there is the broad field of can linings.

Much has been written on high vacua and vacuum technique<sup>36, 37, 38</sup> and it is suggested that those interested in the process of vacuum evaporation first become fully acquainted with the physics of high vacua. Many of the principles and equations of the kinetic theory of gases are important in the design, construction, and operation of vacuum apparatus. Problems which arise can be more readily solved by applying a clearer conception and greater knowledge of vacuum principles.

## Chapter 12

# Silver in Stationary Electrical Contacts

SILVER CONTACTS IN POWER SERVICE

By LYALL ZICKRICK\*

On almost all types of current-carrying electrical apparatus it becomes necessary to provide some means for opening and closing circuits, and for performing this function contact materials must be considered. Silver is probably the most widely used precious metal for electrical contacts. It has the lowest electrical resistivity of any metal and is superior to all others as a conductor of heat, two extremely important factors in the making and breaking of electric circuits.

The part played by contacts in electrical apparatus has been appropriately stated by Kingsbury,<sup>†</sup> who says that no element in an ordinary electrical circuit is so little understood as the contacts, and the accompanying physical and chemical phenomena associated with the interruption and closure of circuits. When these operations are performed, complex reactions may occur, and excessive temperatures can be attained by metal particles and in local areas. These temperatures may be sufficient to melt and vaporize metal and result in chemical reactions with the atmosphere.

Two fundamental duties must be performed by contacts in service. First, it is necessary that the current be carried continuously without excessive heating when the circuit is closed. Secondly, since the prime cause of difficulty in making and breaking a circuit is arcing, it is essential that the contacts dissipate the arc energy of the circuit without undue alteration or destruction of the tip metal.

In consideration of the first requirement, it will be realized that heating at the contact faces is largely dependent upon contact resistance, and unless a metal gives low resistance at the contact, it is unsuitable. One of the important factors affecting contact resistance is the formation of oxide or sulfide films.

Copper is the most commonly used metal for carrying current, and copper contacts are used extensively in heavy-current apparatus. Copper, however, oxidizes rapidly, and the oxide has a very high resistance. For general applications and apparatus where copper is not suited, the use

\* Research Laboratory, General Electric Co., Schenectady, N. Y.

<sup>†</sup> "Use of Noble Metals for Electrical Contacts," E. F. Kingsbury, Trans. A.I.M.E., 1928.

of silver may prove advantageous; and although its cost is considerably higher than that of copper, it is far cheaper than other noble metals. It possesses much greater resistance to oxidation than copper, aside from its superior heat and electrical conducting properties mentioned above. This is, perhaps, best illustrated in Figure 1, where a direct comparison is shown between copper and silver and their change in contact resistance. Sets of copper and silver contacts were exposed to the atmosphere at a temperature of 85 °C over a period of time. At periodic intervals the tips were brought together under a pressure of 20 pounds and their contact resistance measured. Silver, as may be observed, does not under ordinary atmospheric conditions show a rapid change in contact resistance.

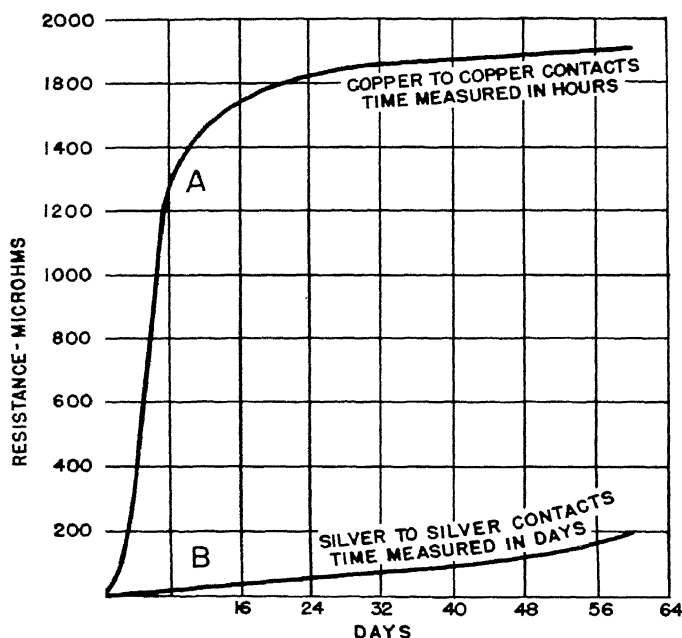


FIGURE 1. Change in resistance of copper-to-copper and silver-to-silver contacts when exposed (not closed) to a temperature of 85 °C. Measurements taken intermittently.

All metal oxides are of high electrical resistivity; in fact, most may be classified as insulators. It has frequently been reported and published in the literature that silver is a good contact material because its oxide is a good conductor. This is not true. Silver oxide has a very high resistance, as has been found from measurements taken on carefully

prepared samples. Values ranging from 40 to 50 megohms/cm<sup>2</sup> have been obtained on pure silver oxide.

Silver oxide, however, is one of the unstable oxides at elevated temperature, and when heated to 300-350 °C it readily decomposes, giving up its oxygen, and becoming pure silver. It is doubtless this property which has been responsible for such an erroneous belief. In the operation of a contact in the presence of silver oxide, sufficient local heat is undoubtedly generated at the point of high contact resistance to decompose any oxide in the path of the current. There are many metallic oxides which show a rapid drop in resistance at elevated temperatures, but they are stable and do not readily decompose like silver oxide.

The function of breaking an electric current introduces different requirements from those of carrying current, and for heavy currents where arcing occurs, silver, on account of its softness and relatively low melting point, is not entirely suitable. Under these conditions it becomes subject to sticking, and the surfaces of the contact tips rapidly erode from the burning of the arc. In certain types of direct-current circuits, silver exhibits a pronounced tendency to build up from one electrode to another. However, in circuits where currents or load requirements are not excessive, pure silver contacts are used widely and in large numbers. Here it is

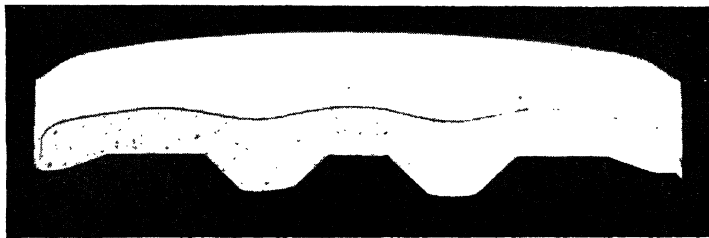


FIGURE 2. Section of steel-backed silver contact button.

possible in many applications to use a simple mechanical construction for making, breaking, and carrying the current. This is not so readily accomplished with metals like copper where a wiping action of the tips is generally required. Advantages resulting from the employment of silver outweigh the small extra cost over alternative base metals. Base metals also, as a rule, require heavier construction and larger sections to perform the equivalent work or to show as high efficiency.

The growing demand for silver as a metal for electrical contacts has caused the employment of many ingenious methods of manufacture for the purpose of reducing the weight or quantity of the silver in actual service. One product which, over the past few years, has grown rapidly in use is the steel-backed silver contact.

In the manufacture of steel-backed silver contacts, a billet of steel and a billet of fine silver are generally used. The two billets are joined together by inserting between them a layer of suitable bonding material such as copper-silver alloy, and fusing at an elevated temperature. The fused or laminated bar is rolled to reduce the thickness and to obtain the sheet stock desired. From the sheet stock, slugs of the composite material are punched, and these are subsequently worked in a coining machine to produce the finished button. This final operation gives the button the desired diameter and provides it with projecting tips on the steel side for welding. The button has a silver top of the proper thickness and radius of curvature; and in addition, the silver extends over the sides of the steel portion so that when mounted, the sides, as well as the top, present a silver surface. An enlargement of a section taken through a steel-backed contact is shown in Figure 2.

The backings for such contact tips are in no way limited to steel, but may be made from any other suitable commercial metal or alloy, such as copper, nickel, or Monel metal.

### Silver Alloys

Among the most extensively used silver alloys for contacts are those of silver-copper. The copper content of coin silver (10 per cent copper) and sterling silver (7.5 per cent copper) increases the hardness of the alloy to a considerable extent, but unfortunately decreases the resistance to film formation or oxidation, and the alloys become somewhat more susceptible to atmospheric corrosion. Where contacts operate with sufficient wiping or sliding action, the film is easily destroyed and the working surfaces remain clean. In installations where there is considerable mechanical action, coin or sterling silver is suitable on account of its greater hardness and consequent resistance to wear. These alloys are useful where atmospheric surroundings are not likely to promote serious oxidation and are free from sulfur.

The electrical conductivity of coin silver may be increased from values of around 70 per cent to approximately 100 per cent by appropriate heat treatment. The silver-rich alloys show decreasing solubility of copper with decreasing temperature. Johanssen and Linde\* determined the electrical conductivity of a number of alloys after long periods of annealing at 750 °C and 350 °C followed by quenching. Solubility limits of 8.2 per cent copper at 750 °C and 1.7 per cent copper at 350 °C were found. The effect of the decrease in solubility upon the electrical conductivity of coin silver is very pronounced, as may be seen in Figure 3.

A great number of alloys of silver are used commercially for contacts, many of which are patented compositions. They have been marketed

\* C. H. Johanssen and J. O. Linde, *Elektrische Leitfähigkeit und Gustandschaubild der Kupfer-Silberlegierungen*, *Z. Metallkunde*, 20, 443 (1928).

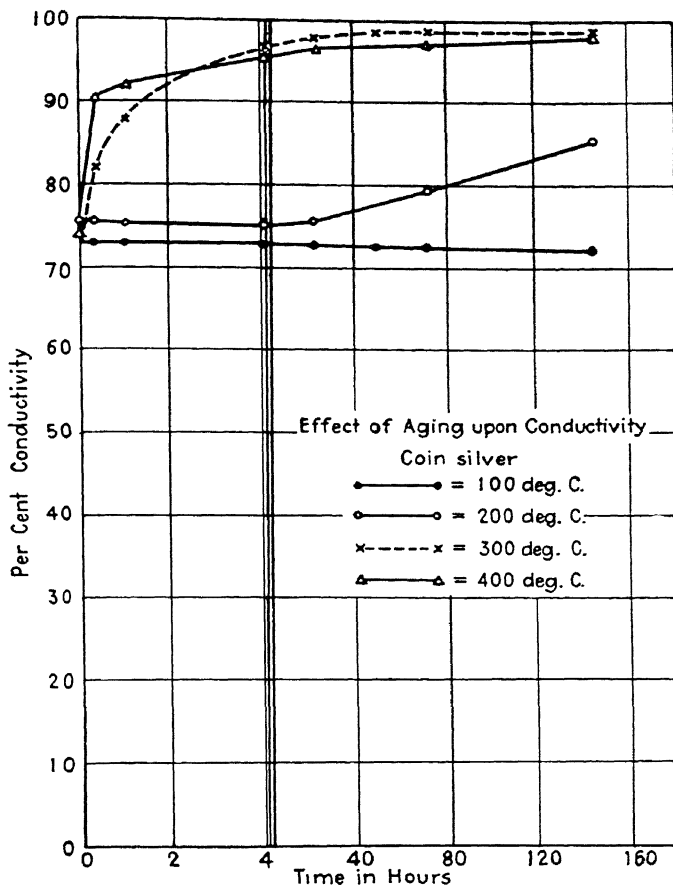


FIGURE 3. Effect of aging upon conductivity of coin silver.  
(T. C. Jarrett, *Metals and Alloys*, Dec. 1936, p. 309.)

as possessing especially desirable properties and for particular applications. Among these may be listed a few of the following in which silver constitutes an appreciable part of the total metal.

Silver-cadmium	Motor starters
Silver-graphite	Railroad signal relays
Silver-molybdenum	Motor starters, arc-resisting
Silver-tungsten	Motor starters, arc-resisting
Silver-platinum	} Special applications, and as substitutes for expensive noble metals.
Silver-gold	
Silver-palladium	

For good wear resistance and additional hardness, silver powder may be sintered with other metal powders. Such materials are generally of low electrical conductivity and give high contact resistance which necessitates increased contact pressure. They are, however, frequently employed where arcing conditions are severe or serious trouble with sticking is encountered, such as in high inductive circuits or circuits where a high inrush current occurs. The disadvantage of low conductivity and high contact resistance may be overcome where the service is heavy-duty by using auxiliary contacts of silver that close after and open before the arcing tips. Sintered silver-molybdenum of approximately 40 per cent silver is a suitable material for such applications. Silver powder and molybdenum powder are mixed together thoroughly, pressed in a bar or to a desired shape, and sintered at an elevated temperature in a hydrogen atmosphere. Silver-tungsten may be produced in the same way. These materials combine the desirable properties of silver with the high-temperature and arc-resisting properties of molybdenum or tungsten. They are expensive and are generally used as a plate or insert mounted on a base metal support.

### Silver Contacts in Switchgear Service

Copper has long been so extensively used for a conductor of electric current that the electrical industry naturally employs its current-carrying ability for points and switches both in air and under oil. However, its pronounced tendency to oxidize at moderately elevated temperatures, not only in air but under oil as well, introduces an objectionable surface. The result may be excessive heating, sufficient to anneal and soften the copper or damage the contact surfaces. This is especially noticeable in apparatus designed to operate at high current densities, where the sliding or wiping action of adjacent surfaces in making or breaking a circuit is insufficient to remove or wear away the oxidized surface and prevent the temperature increase.

Table 1.  
No. of days to reach 5  
times initial contact resist-  
ance at 85 °C

Material	AIR	OIL	terms of fine silver
Fine silver	21	19	1.0
Coin silver	4	14	1.6
Copper	1	5	2.3
Nickel	16	1	36.0
Tungsten	7	—	50.0
Tin	8	7	3.2

From the standpoint of such applications, silver is an ideal contact metal and shows a minimum of increase in electrical resistance with length of service. Tests have shown that fine silver either in air or under oil requires approximately twenty days to reach the same resistance as that attained by copper contacts in about one day under the same condition of temperature and pressure.

Table 1 gives the time required for contacts of various materials to reach five times their initial contact resistance, both in air and under oil:

Although the superiority of silver contacts over copper contacts cannot be stated in definite figures, it may be safely estimated that silver contacts can usually be expected to give satisfactory service for a longer time than copper. Silver contacts permit a higher temperature for current rating than plain copper contacts. For silver contacts, no difficulties should be experienced with a 50 °C temperature rise from a 40 °C room temperature if fine silver of 99.9 per cent purity is used.

Results of tests showing temperature rise for silver-to-silver and copper-to-copper surfaces under oil where no arcing or abrasion is present are given in Figure 4.

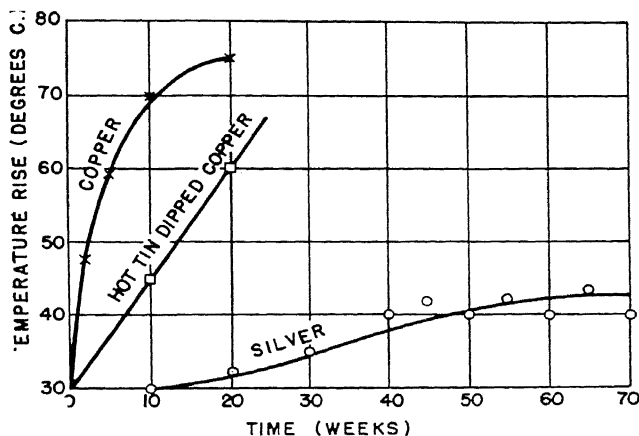


FIGURE 4. Time-temperature curves for different contact materials. Intermittent duty at 600 amperes in oil.

In general, non-arcing silver contacts may be designed to operate at somewhat lower contact pressures than copper contacts. Some idea of the differences in contact resistance for various pressures may be gained by noting the curves given in Figure 5. Data are given for both line contacts and surface-to-surface contacts. The curves show change in contact resistance for the particular conditions of test. The results would be altered or modified somewhat by different circumstances or in a different application.

A great number of wedge and finger type contacts used on circuit breakers have surfaces faced with pure silver. A layer to a depth of .003 in. has been stated as sufficient for many applications. Greater current densities can be handled when silver is used, and the apparatus



can be designed and built so as to require only occasional or infrequent attention.

It is common practice to use silver as a contact metal in large current-carrying air circuit breakers. In this type of breaker the current is

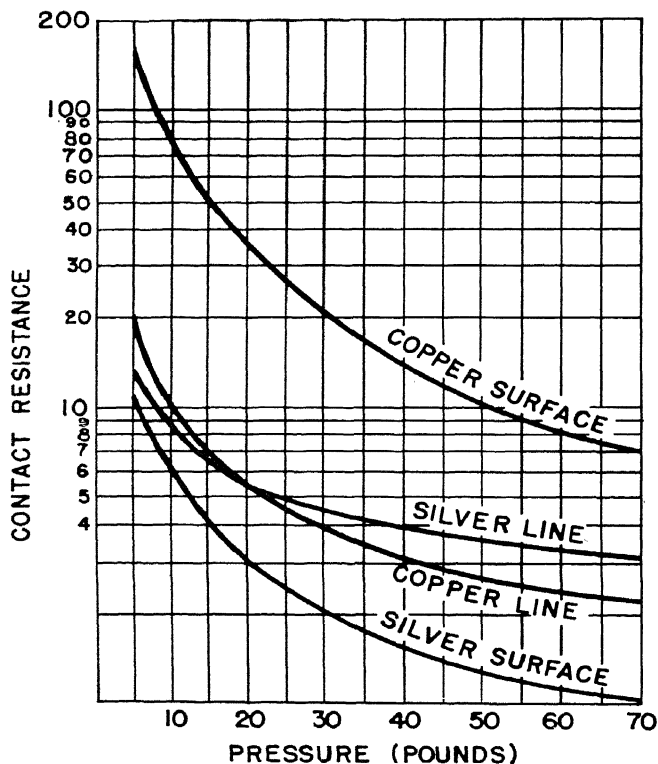


FIGURE 5. Initial contact resistance curves with varying pressure for copper-to-copper and silver-to-silver line and surface contacts.

Surface contacts:  $1'' \times \frac{3}{8}''$ .

Line contacts:  $1''$  long  $\times$   $3''$  radius.

interrupted on separate arcing tips and carried during the period of operation on silver bars mounted as inserts in the breaker mechanism. Such a breaker is illustrated in Figure 6.

Thin silver facings of laminated or inlaid construction are used for the contact area in many disconnecting devices and various types of

switch blades. They are so arranged and constructed that only the effective working surfaces consist of silver.

### SILVER-MANGANESE CONTACTS \*

BY C. PETERSON †

Studies made by ourselves and others<sup>1</sup> have indicated how the metal transfer characteristics of fine silver and high silver alloys are influenced by circuit conditions when contact points made of these materials are

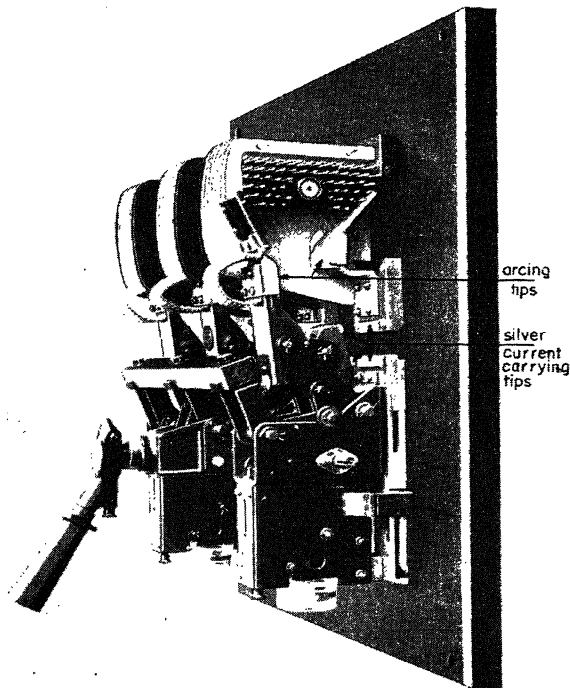


FIGURE 6. Eight hundred-ampere, air circuit breaker, showing silver current-carrying contact tips.

used to open and close a D.C. circuit. In general, a slight amount of arcing is beneficial<sup>2</sup> because it produces a type of transfer which is more diffuse and less likely to cause "hanging" or "hooking together" of the cooperating contacts which form a pair. This "hanging" or "hooking together" of contacts is a type of sticking which is mechanical in nature

\* These alloys contain 5 to 11 per cent manganese.

† H. A. Wilson Co., Newark, N. J.

as contrasted with sticking due to fusion welding. In some common devices, such as automotive-type voltage regulators, the circuit conditions are frequently such as to produce an undesirable type of transfer when fine silver contacts are used as a coöperating pair. We have found that, if the anode contact is made of silver-manganese alloy and the cathode of substantially fine silver, a desirable type of transfer can be secured over the relatively broad range of current values encountered in these devices. The contacts referred to control the generator field current.

The exact role which manganese plays in these effects is not definitely understood, but it is evident that it promotes arcing to a degree sufficient to obliterate the local cones and craters which would otherwise have been formed. Arcing tends to produce transfer from cathode to anode. Silver is thus deposited on the silver-manganese anode and the tendency is to create a pair of fine silver contacts. A pair of fine silver contacts produces transfer in the reverse direction, from anode to cathode, under identical circuit conditions. With polarized contacts operating under these conditions the net amount of transfer is negligible over long periods of operation. The advantage of polarized contacts is lost when the current interrupted is increased beyond the point where a pair of contacts made of cathode material would transfer in the cathode to anode direction.

#### SILVER CONTACTS IN TELEPHONE SERVICE

BY LYALL ZICKRICK

Contacts on telephone apparatus are subjected to relatively low operating voltages, currents, and pressures. It is for this reason that films of dust and corrosion products of relatively small thickness may introduce sufficient resistance to affect contact operation adversely.

Some idea of the extent to which our modern communication systems are dependent upon electrical contacts is given by Schumacher.\* In an ordinary dial system call between subscribers in a large city the number of precious metal contacts that must operate reliably involves about 300 relays and over 1000 pairs of contacts. In a call between New York and San Francisco, about 1500 additional pairs of precious metal contacts must perform dependably for satisfactory transmission. In some years the communication systems have required more than 100,000,000 pairs of contacts for different kinds of telephone apparatus.

In general, there are two main classes of contacts used in dial telephone apparatus—those of the sliding type in which the brush slides over the contact, and those of the percussion type in which the two elements of the contact are brought together head-on.

Recently, silver plate has been tried as a substitute for brass on sliding contacts and appears to provide improved transmission characteristics. In relay contacts, the currents are higher on the average, and

\* Schumacher and Ellis, *Metal Progress*, 36, 617 (1939).

loss due to erosion is an important factor. For this reason, silver contacts on relays have been used in the form of a button of silver welded on the contact spring.

Silver, in common with other noble metals such as platinum, palladium, and gold, has an advantage over base metals in that it does not readily form an oxide film at room temperature by reaction with oxygen in the atmosphere. It has the disadvantage, however, that it does form a sulfide film very rapidly. Although sulfide films on silver appear to be more readily broken down during operation of the contact than films formed on base metals, they are nevertheless, under certain conditions, a distinct disadvantage.

Silver forms silver sulfide on its surface on exposure to atmosphere more rapidly than copper oxidizes at room temperature. The presence of silver sulfate has been reported in the film formed on silver in industrial atmospheres where sulfur dioxide concentrations and humidities are very high. The part which these films play in contact performance is not completely understood, but it may be of interest to review certain distinctive properties of silver sulfide.

The resistivity of silver sulfide is very much lower than that of the compound composing the films which form on the general run of contact metals. For example, the resistivity of pure silver sulfide at room temperature is lower by a factor of one millionth than that of pure cuprous oxide. The resistivity change of silver sulfide with temperature is also of interest. It decreases by a factor of the order of one thousandth in going from room temperature to a temperature of 173 °C, where the beta silver sulfide undergoes a transition to the alpha form and the change is accompanied by a sudden decrease in resistivity. Another unique property of silver sulfide is its tendency, when heated in contact with silver, to form trichites, or hair-like filaments of silver, through the film and out into the air. Silver sulfide is considerably softer and more plastic than tarnish films on base metals, being of the order of hardness of lead.

Although formation of silver sulfide is a definite disadvantage from the viewpoint of efficient contact operation under some circumstances, it is probable that the relative superiority of silver as a contact material over base metals such as copper is largely due to the unique properties of silver sulfide, particularly when the contact is subjected to high voltages, currents, and pressure.

In the case of sliding contacts, the building up of resistance due to film formation does not appear to be such an important factor, possibly because the abrading action of the sliding brush removes the film from the brush track, but it is still a disadvantage in that the development and removal of film cause acceleration in wear.

In recent years, progress has been made in the development of methods for preventing the tarnishing of silver. Unfortunately, the more success-

ful of these processes involve the formation on the surface of the silver of an invisible film of high electrical resistance, which impairs the serviceability of the metal for use in telephone circuits.

Relay contacts are protected from tarnish to some extent by the fact that the relays are enclosed within metallic cases. From the standpoint of economy, the replacement of the more precious metals by silver would be desirable. It is unlikely, however, that general use of silver could be considered until the problem of prevention of sulfide formation is solved by a method which does not involve changing the desirable low-resistance characteristics of a clean silver surface.

### SILVER CONTACTS IN TELEGRAPH SERVICE

By F. H. CLARK \*

The desirable characteristics to be obtained in a contact material fall chiefly into five classes, the relative importance of each depending on the nature of the service to which the contacts are to be applied:

- (1) low resistance,
- (2) freedom from corrosion at elevated temperatures,
- (3) high melting point,
- (4) high arc potential,
- (5) mechanical hardness.

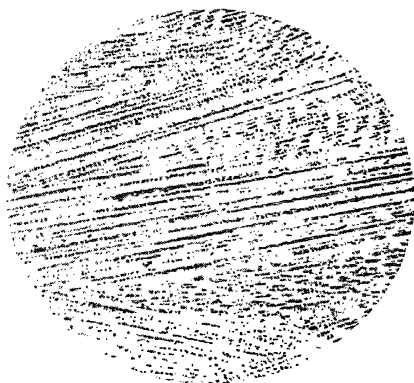
While all these factors are interrelated to some extent, they may be considered independently in evaluating the suitability of any one material for a specific application. Reasonably low resistance is usually of paramount importance and includes the volume resistivity of the material as well as the resistance of the contact surfaces. The volume resistivity, if high, can be allowed for in the design of the contact by employing a large cross-section in order to keep the current density low and thermal radiation high. This is not so easy, however, if the contact tends to have a high surface resistance, since electrical contact occurs only over a very minute area where the current density is likely to be quite high. It is absolutely essential in some applications that the contact surface offer not only a lower resistance but a uniform resistance as well, so that materials must be used which are free from chemical changes at the surfaces.

If atmospheric corrosion produces chemical salts which are different in resistance from the original clean contact, the circuit may be interrupted, and it then becomes necessary to clean the contacts to restore proper circuit continuity. Such maintenance is often costly if required too frequently.

In addition to the problem of atmospheric corrosion, which may occur at normal room temperatures, is the further danger of chemical change

\* Metallurgist, Western Union Telegraph Co., N. Y. C.

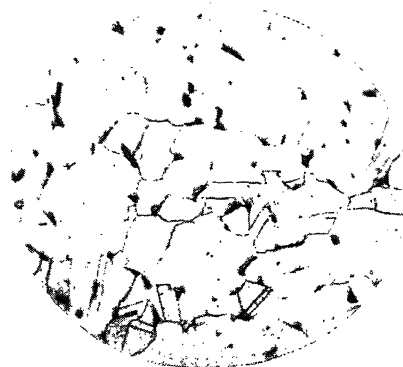
% Zn      11.7  
 % Ag      88.3  
 Condition   As cast



% Zn      11.7  
 % Ag      88.3  
 Condition   Annealed 5 hr. at 500 °C.



% Zn      26.0  
 % Ag      74.0  
 Condition   Cold-worked and annealed.



*Magnification:*  $\times 100$ .

*Etchant:* 15% nitric+85% acetic acids.

FIGURE 7. Microstructure of tarnish-resistant silver-zinc alloys.

at the high temperatures produced by electrical discharges. Just what temperature is reached during arcing and sparking, as a result of contact operation, is not definitely known; but it has been established that such refractory materials as tungsten, molybdenum and osmium are sometimes vaporized under these conditions. Many materials, satisfactory on circuits where no such discharges occur, form insulating oxides in an arc which adhere to the contact surface after cooling. This oxide film may be destroyed by high mechanical pressure or by a high voltage on some types of application, but quite frequently the nature of the equipment makes it impractical.

Materials having high melting points and high arc potentials are essential in applications where the circuit current to be interrupted at the contacts is high. Such materials as silver and copper, for example, if operated as contacts at high current levels, will fuse together. For this reason it is sometimes necessary to use palladium or more refractory metals. Roughly speaking, silver and silver-copper alloys are satisfactory only at levels below .300 ampere; palladium can be operated up to .900 ampere and osmium up to 1.700 ampere. Higher current levels require the use of mitigating means, such as arc suppressors, to avoid frequent contact maintenance.

The use of coin silver as an electrical contact material is satisfactory where current and voltage characteristics are high enough to break down the corrosion products accumulated on the surface. But in industrial atmospheres where metallic sulfides form readily, a high surface resistance on the contact has prevented their use on circuits where currents and pressures are too low to break through the corrosion products.

To improve this condition, the Western Union Telegraph Company undertook an investigation to develop a contact material that would maintain a low surface resistance over a period of years on exposure to the air while undergoing only an occasional make and break.

A preliminary survey was made of a series of binary alloys of silver with other metals and corrosion tests were carried out by immersion of the sample in sodium polysulfide solution. (See "Tarnish Resisting Silver Alloys," Louis Jordan, L. H. Grenell, and H. K. Hershman, U. S. Bur. Standards Tech. Paper 348.) A comparison of the time required to discolor the sample with the time for darkening coin silver was noted in a sodium polysulfide solution similar to that required in A.S.T.M. Designation B33-21 (see A.S.T.M. Standards 1936, page 671). The silver-zinc alloys showed marked superiority over other alloys in preventing the formation of silver sulfide, which is believed to be the chief cause of high surface resistance on silver exposed to the atmosphere.

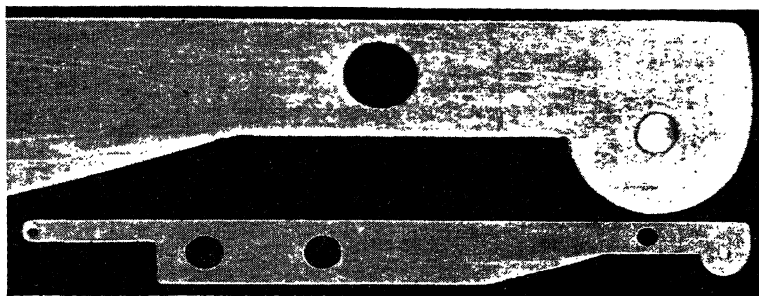
Increase in zinc content decreased the tendency to form silver-sulfide as shown in the following table. The ingots were carefully polished, immersed in sodium polysulfide solution for short periods, removed, rinsed, wiped dry and examined. At the end of one minute, the copper-

silver alloys were badly tarnished. The zinc-silver alloys after 30 minutes immersion were colored as follows:

7.2%	zinc—straw color
14.7%	zinc—light straw color
21.7%	zinc—light tint
29.4%	zinc—no perceptible tarnish
31.1%	zinc—no perceptible tarnish
32.2%	zinc—no perceptible tarnish

Not only was the tarnish resistance an important factor, but workability had to be taken into consideration to insure that the alloy could be drawn into the form of wire, from which contacts could be economically made by cutting the wire into short pieces, inserting them into holes of the contact springs and securing them by peening the ends. An alloy of 25 per cent zinc marks about the upper limit of zinc permissible for drawing into wire form. This composition gave sufficient corrosion resistance on exposure to the atmosphere and was adopted as a standard.

Magnified 3.5 times



Actual size

FIGURE 8. Silver-zinc contact mounted on spring.

Contacts of silver-zinc have now replaced silver-copper or coin silver not only because of their low surface resistance on exposure to the atmosphere, but also because they are more economical. As stated above, their low melting point makes them suitable only for operation at low current levels. An upper limit of 300 milliamperes has been established for their use, as above this limit arcing and melting may occur. One of the interesting aspects of the silver-zinc alloy is that, although the contact darkens on exposure to the atmosphere, it has been found to give satisfactory service when used on jacks in carrier circuits where currents are exceedingly small. As an example, the contacts have given uninterrupted service over a period of two years on jacks in carrier circuits operating at  $-30$  decibels where  $0$  decibels is equivalent to  $1$  milliwatt in



Western Union practice. This network operates at 600 ohms impedance.

The principal applications for this material have been for contacts for jacks and telegraph relays. Figure 8 shows a contact of 80 per cent silver 20 per cent zinc which has been mounted on a spring by peening the ends to give a hemispherical surface. This contact operates against a similar spring and contact and is mounted in a relay.

At the present time distributors for multiplex telegraph circuits are equipped with face plate segments made of bronze, over which pass copper brushes moving at high speed. Tests have been carried out on face plate segments made of a silver-zinc alloy. This substitution appears to decrease the wear and erosion and thereby increases the life of the distributor.

## Chapter 13

### Silver in Moving Electrical Contacts

By STANLEY B. WILTSE \* AND HAL M. PARSHALL †

#### The Use of Brushes

All dynamo-electric machinery consists of a stationary element or stator and a rotating element or rotor. In general both of these elements carry conductors through which currents flow. In many cases it is necessary to feed current to or from the rotor conductors by means of sliding contacts. In some cases the currents in the rotor conductors are set up by induction, as, for example, in the case of the induction motor. However, even in the case of the induction motor, it is frequently desirable to regulate the currents in the rotor circuit in order to obtain speed or torque control. Under these circumstances the motor is usually of the wound rotor type and provision is made to insert variable resistance in the rotor circuit. The variable resistance is usually external to the motor and is arranged to connect by means of sliding contacts to slip rings acting as terminals for the rotor circuit and mounted on the rotor.

In alternating-current machinery the rotating current-collecting devices generally consist of metallic slip rings, usually of bronze alloy or steel. The current carried across the sliding contact may be either D.C. or A.C., depending upon the type of machine. In the case of an alternator or synchronous motor with revolving field the current is D.C. In the case of a synchronous converter, induction alternator or induction motor the current is A.C.

In direct-current machinery and in some alternating-current machinery the rotating collector is a commutator consisting of copper segments insulated from each other by mica.

Connection is made to the rotating collectors by means of brushes. Brushes have a wide range of composition. In general they always contain some graphite to act as a lubricant to cut down wear and scoring. Probably the most generally used brushes consist of graphitized carbon. When brushes must operate at high current densities they are frequently composed of a mixture of some metal and graphite. The most commonly used metal is copper. Frequently brushes composed principally of copper and graphite also contain small amounts of lead and tin to secure some desired characteristic.

\* Professor of Electrical Engineering.

† Silver Research Fellow, Rensselaer Polytechnic Institute.

## Brush Grades

Anyone who looks through the catalogs of brush manufacturers will immediately be impressed by the many different grades of brushes listed, each for specific applications. There will be listed many different grades of carbon brushes of varying degrees of hardness, and many grades of metal graphite brushes containing different amounts of metal. For example one prominent brush manufacturer lists as many as 59 distinct grades of brushes divided into five classifications: carbon graphite, electro-graphitic, natural graphite, resin-bonded graphite and metal-graphite. These various grades are each recommended for various peripheral speeds of collector with various degrees of abrasive action and for various brush current densities. The resin-bonded brushes have a higher conductance radially than circumferentially because of laminated construction and are recommended for use in commutating machines where commutation conditions are severe.

## Primary Considerations

Two primary considerations in the operation of sliding contacts are the voltage drop across the contact between the brush and collector ring and the wear of either the brush or the collector ring.

The voltage drop is important from two viewpoints. First, the product of the voltage drop across the contact and the current flowing across the contact represents a power loss and subtracts from the efficiency of the machine. Secondly, the power loss at the contact produces heat which not only may cause severe local heating but may contribute to the general heating of the machine, and must be allowed for in the design.

Where the only function of the collecting device is to conduct current to or from the rotor, as is the case with slip ring types of machines, minimum voltage drop across the contact is desirable. Where the collecting device serves some additional function, as in the case of a commutator which serves as a means of reversing the rotor current, it may be desirable to have a fairly high contact drop to assist in the current reversal.

Mechanical wear is also important. If the brushes wear rapidly they must be replaced frequently and their replacement cost may be high. If the collector rings or commutator wear rapidly, repair costs may be an important expense item. In addition, the machine may have to be removed from service while repairs are made. High friction losses may accompany high mechanical wear. These losses will subtract from the efficiency and contribute to the heating. In general minimum wear at the brush contact is always desired.

## Theories of Brush Contact Drop

Although sliding contacts have been used ever since the first development of the dynamo, no completely satisfactory theory has ever been evolved to explain exactly what happens under a brush contact. A

number of different theories have been advanced to explain the phenomenon. One holds that the current passes across the contact as an arc; another, that conduction across the contact is by virtue of thermal emission and thermal ionization; another, that conduction takes place through small pinnacles of the brush which make point contact with the collector ring, and that with wear these pinnacles are continually being destroyed and new pinnacles established. Another theory states that conduction takes place through the semi-insulating oxide film at the points of contact. A more elaborate theory divides the brush surface into three zones, called respectively the Hertz surface, the dust zone and the arcing zone. Under the Hertz surface, conduction of the current is partly by direct contact of brush to ring, partly by contact across conducting dust between the brush and the ring, and partly by arcing, because of the contact separation caused by non-conducting dust particles or by the relative motions of the contact surfaces. In the dust zone, conduction is by means of conducting dust and arcing. In the arcing zone conduction is by arcing alone. All these theories are supported by considerable experimental evidence. None of them completely explains the phenomenon for all conditions. Careful perusal of the published results of many experimenters and of the theories which have been evolved must inevitably lead one to the following conclusions:

1. The phenomena which occur during conduction across a sliding contact are most complex and are influenced by a great many variable factors.

2. Although many different theories have been evolved to explain the phenomena, none in itself offers a completely satisfactory explanation and it is probable that several of the theories may be simultaneously involved.

3. There is still a great deal of experimental work to be done before any definite explanation of the phenomena can be advanced.

It may be said at the outset that in this chapter the authors have made no attempt to substantiate any of the existing theories. They have simply gathered additional data in a field which so far as they know has hitherto been unexplored. It is hoped that this information may be added to that obtained by other experimenters and that it may ultimately help to establish a definite answer to the problem.

### **Brush Wear**

There is a similar lack of definite information as to the process of brush wear. Investigators have noted that the brush wear for brushes carrying no current differs from that for brushes carrying current. They have also noted that with D.C. operation there is a definite polarity effect at the brushes and that the wear of positive and negative brushes operating simultaneously on the same rings under the same conditions is not the same. They have also noted that this polarity effect seems to

depend upon the brush and ring materials. Indications are that electrolysis also is involved in the brush problem.

### **Establishment of Silver Research Fellowship at Rensselaer Polytechnic Institute**

For several years previous to June, 1937, a study of the sliding electrical contact had been conducted at Rensselaer Polytechnic Institute as a thesis project. This study had been concerned only with the electrical characteristics of carbon and copper-graphite brushes operating on copper slip rings. In addition to considerable experimental work, the published results of other investigators were examined and an effort was made to correlate these results with the results obtained at the Institute.

One very definite conclusion drawn from the results of this investigation was that many of the undesirable characteristics encountered in the operation of commutators and slip rings were caused by the contaminating film formed on the surfaces of these sliding contacts. This conclusion coincided with conclusions reached by other investigators and was borne out by the fact that brush manufacturers, in listing brushes, graded them according to their abrasive action in removing the contaminating film.

It seemed logical that the next step should then be to find some material for use in slip rings and commutators which would not develop an undesirable contaminating film in ordinary atmospheres.

Silver is a better electrical conductor than copper. In addition the contaminating film formed on a silver surface in ordinary atmospheres is a fairly good electrical conductor. However, in comparison with other commercial conductors, silver is expensive. If it could be used economically it seemed like a promising material to investigate.

It was at about this time that the American Silver Producers' Research Project was formed to investigate possible new uses for silver.

The work at Rensselaer Polytechnic Institute was called to the attention of the directors of the Project, and the Institute was chosen as one of the participating institutions. Dr. Matthew A. Hunter and Professor Stanley B. Wiltse were chosen as co-directors of the Project at the Institute and Dickerson P. Miles was appointed Research Fellow.

### **General Description of Equipment and Tests**

The original idea was to use collector rings or commutators of either pure silver, or some other metal with a pure silver facing, operating with conventional carbon or metal-graphite brushes. To this end a pure silver ring and a commercial copper ring were arranged on the same shaft to be motor driven. Brushes were mounted in commercial brush holders to make contact with the rings. The brushes and rings were connected to form a series electrical circuit through which direct current was passed. The copper ring was to be used as a control with which to compare the results obtained in the operation of the silver ring.

However, shortly after the investigation had started, one of the prominent brush manufacturers presented the Project with a few experimental brushes composed of approximately 90 per cent silver and 10 per cent graphite. In the course of the investigation these silver-graphite brushes were operated on the copper ring. It was discovered that after a short period of operation the copper ring developed a very definite silver coating on the brush track, and that the contact drop fell to a very low value, approaching that of a silver-to-silver contact. This discovery almost immediately changed the whole course of the investigation. If the silver track could be laid down by the use of silver brushes it would eliminate the necessity for pure silver or silver-faced collectors and the cost would be materially decreased. In addition it might be possible to adapt silver brushes to existing equipment and thus open an immediate market for silver. Thus the pure silver ring now became the control ring and the copper ring the experimental ring. Until this time all experimental work had been done in room atmosphere with no attempt to control temperature or humidity. Unless the preliminary tests indicated the possibility of favorable results there was no use in constructing rather elaborate equipment for control test conditions.

On the basis of the favorable results obtained in the preliminary tests, it was considered worth while to construct more elaborate testing equipment. Consequently an air-conditioned cabinet was constructed in which the original test rings and a second set of test rings could be operated. The air circulating equipment was constructed as a closed system so that it would be possible to introduce various types of contaminating atmospheres. Investigation showed that the silver brushes could be operated on copper slip rings at nominal current densities of as high as 400 amperes per square inch with very low heating and very low voltage drop.

Since such high brush current densities seemed practical, it appeared that silver-graphite brushes should be applicable to low-voltage, high-current machinery. An application which at first looked promising was that of the automobile starter motor and this field was investigated. It was found that so far as voltage drop was concerned there was little, if any, advantage in using silver-graphite brushes in place of the customary high copper content copper-graphite brushes. Wear tests by one of the prominent brush manufacturers did show a much longer life for silver-graphite brushes than for copper-graphite brushes. However, under normal conditions, copper-graphite brushes would outlast a car, and silver-graphite brushes would, therefore, offer no practical advantage. In addition it was found that, in a competitive field such as the automobile industry, it would be difficult to persuade the manufacturer to pay more for silver-graphite brushes when copper-graphite brushes were sufficiently satisfactory. Thus the investigation of the use of silver-graphite brushes in the automotive field was discontinued.

The investigation of brushes operating on slip rings was continued. As the investigation has progressed, the program has been expanded to include numerous compositions of copper-graphite and silver-graphite brushes. An assembly consisting of six 8-inch diameter slip rings was built. Two of the rings were of bronze alloy, two of steel and two of cast iron. These were arranged to be driven at either 1200 r.p.m. or 1800 r.p.m. to give peripheral speeds at the ring surfaces of approximately 2500 f.p.m. and 3600 f.p.m., respectively. Another assembly of two 19-inch diameter steel rings was constructed, driven by an adjustable-speed D.C. motor to give peripheral speeds of as high as 10,000 f.p.m.

In June, 1939, D. P. Miles, who had been Research Fellow for two years, left to accept a position in industry. Hal M. Parshall was then appointed research fellow and has since continued the experimental work.

During the whole progress of the investigation the Project has kept in close touch with prominent members of the electrical industry in order that the work might be held to a practical basis. Industry has been most willing to co-operate, not only by offering valuable suggestions and advice but by donating equipment and materials.

### Procedure

In the early part of the investigation attention was devoted principally to the voltage drop across the sliding contact, since the voltage characteristics could be determined in a relatively short time. Wear measurements would require test runs of comparatively long duration. Unless the volt drop characteristics were favorable, further tests might not be warranted. As the investigation progressed it was evident that the volt drop characteristics were favorable and the program was expanded to include wear tests.

In general the procedure has been to make periodic voltage drop and wear measurements throughout the duration of a test run with the current, brush pressure, room temperature and humidity, and speed approximately constant. Tests have been run with different values of nominal\* brush current density, with different speeds, with different brush pressures and with high and low humidity.

A large amount of data has been obtained which will be discussed and analyzed as it is presented.

## TESTS OF GRAPHITE AND METAL-GRAPHITE BRUSHES ON COPPER AND SILVER SLIP RINGS

### Description of Tests

The tests of graphite and metal-graphite brushes on copper and silver slip rings were conducted in the air-conditioned cabinet. The cabinet

\* By *nominal* current density is meant the brush current divided by the brush area. Because of the imperfect contact between brush and ring the actual contact area is less than the brush area and, therefore, the *actual* current density may be considerably greater than the *nominal* current density.

temperature was held at approximately 21 °C, the temperature variation never exceeding 2 °C. With the exception of one short series of tests conducted to indicate the effect of variation in humidity, the tests were conducted under conditions of approximately 35 per cent humidity. The maximum variation in relative humidity was 10 per cent.

Since the principal use of *copper* in sliding contacts is in commutators it was decided to make the initial tests with direct current, and at the conclusion of these tests to make further tests with alternating current. As the tests have proceeded, new angles of the problem have continually presented themselves. As a result, up to the time this was written, no opportunity had been found to conduct tests with alternating current.

The graphite brush used for comparison purposes was made by the National Carbon Company, No. 259, an electrographitic type. It is rated at 60 amperes per square inch and is recommended as a general purpose grade for D.C. generators, motors and rotary converters in normal and heavy-duty service. It is also recommended for trolley bus motors.

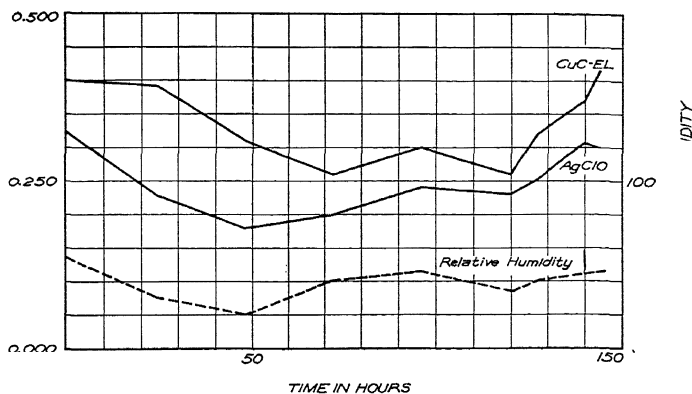


FIGURE 1. Effect of relative humidity on volt drop across brush and brush contact.

Brush pressure 3 p.s.i.

Brush current density 400 amp/sq in

Three grades of copper-graphite brushes were tested. One of these grades consisted of 54 per cent copper, 8 per cent lead and 38 per cent carbon. It was used in the earlier tests for the determination of volt-ampere characteristics. No wear measurements were made on this brush. A second copper-graphite brush tested is designated in the tables as CuC-EL. Its composition is 80 per cent copper, 10 per cent lead, 5 per cent tin and 5 per cent carbon. It is rated at 150 amperes per square inch and is recommended for use on collector rings of rotary converters and for low-voltage plating generators. The third copper-graphite brush



tested was composed of 90 per cent copper and 10 per cent carbon. It is designated in the tables as CuC10.

Four grades of silver-graphite brushes were tested. Two of these grades were supplied by different manufacturers but were manufactured by the conventional process. They are designated in the tables as AgC62 and AgC10. The figures in the designations indicate the percentage of carbon, the remainder being silver. The remaining two silver-graphite brushes designated as AgC10H and AgC5H were supplied by another manufacturer and were manufactured by a new process called the ductile metal powder process. The figures in the designations indicate the carbon percentage, the remainder being silver.

With the exception of a few tests at 1260 f.p.m. the test runs were conducted at a ring peripheral speed of 1850 f.p.m. The speed, the brush pressure and the brush arrangement are indicated in the tables.

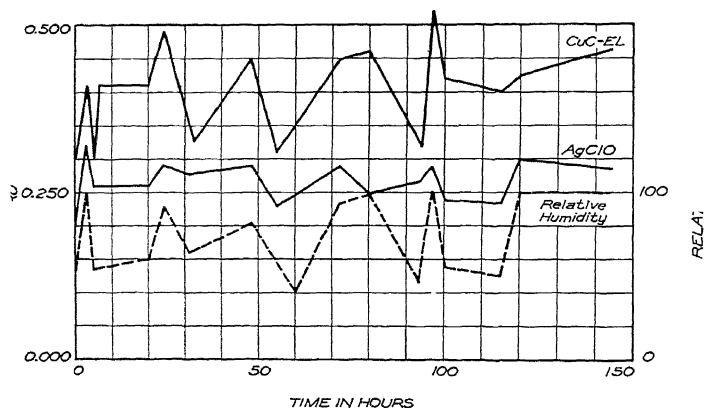


FIGURE 2. Effect of relative humidity on volt drop across brush and brush contact.

Brush pressure 3 p.s.i.

Brush current density 400 amp/sq in

### Humidity Test

A single series of tests was conducted to indicate the effect of variation in humidity on brush wear and voltage drop. These tests indicated that in the case of both copper-graphite (CuC-EL) and silver-graphite (AgC10) brushes the volt drop varied similarly to the relative humidity, increased humidity resulting in increased volt drop. The tests also indicated that the voltage drop at the silver-graphite brush was affected to a lesser proportionate extent by humidity changes than was that at the copper-graphite brush. Figures 1 and 2 illustrate the results of the tests. In general the volt drop curves are quite similar in shape to the

curve of relative humidity. Further investigation of this phase of the problem seems desirable.

### Volt-Ampere Tests

Figures 3 and 4 illustrate typical volt-ampere characteristics for brushes of various types operating on copper slip rings. For comparison purposes a volt-ampere characteristic for the AgC10 brush operating on

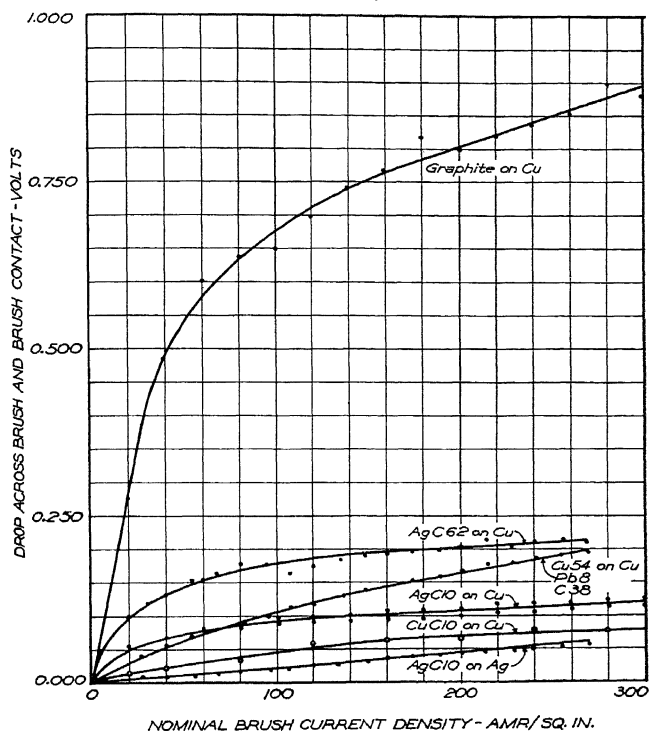


FIGURE 3. Volt-ampere characteristics of brushes of various types operating at positive polarity on slip rings with direct current. Brushes considered positive when current flow is from brush to ring.

a silver ring is also shown. It should be pointed out that these curves are only indicative and cannot be used to determine exactly what voltage drop is to be expected for a given brush at a given current density. During the investigation many such characteristic runs were made. It was found that the ring seemed to develop a surface film which was characteristic for the particular current density at which the brushes had

been operating. It was also found that the volt-ampere characteristic determined after a run at one current density differed from the volt-ampere characteristic determined after a run at some other current density. However, the curves do illustrate the general shape of the volt-

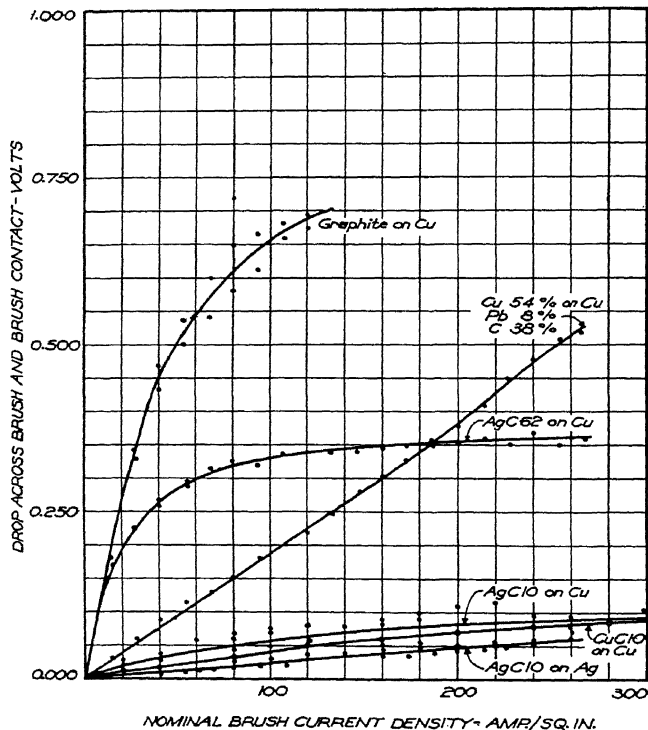


FIGURE 4. Volt-ampere characteristics of brushes of various types operating at negative polarity on slip rings with direct current. Brushes considered negative when current flow is from ring to brush.

ampere characteristic for a given type of brush and also give an idea of the order of magnitude of voltage drop to be expected.

It will be noted that, with the exception of the AgC10 brushes operating on a silver ring, polarity effect is evident to a greater or lesser degree, and that in general the curves exhibit a saturation characteristic.

#### Voltage Drop and Wear Tests with Copper Rings

Tables 1 and 2 include voltage drop and wear data as recorded for the various types of brushes tested on copper rings at 1850 f.p.m. at

three different current densities. Values for graphite brushes at 400 amperes per square inch could not be obtained because of the severe heating ensuing at such a high current density. The data in Table 1 were obtained with positive and negative brushes tracking (operating on same path). The data in Table 2 are for the same brushes operating under the same conditions except with the positive and negative brushes not tracking. Except where otherwise noted, the data presented represent continuous runs of from 131 to 233 hours, the length of run being determined by the amount of brush wear.

Table 1.

Brush Material and Polarity	Copper Rings: 1850 f.p.m. Brush Pressure: Graphite 2 P.S.I. All Others 3 P.S.I.			Brushes Tracking		
	—60 Amp/Sq In— Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)	—120 Amp/Sq In— Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)	—400 Amp/Sq In— Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)
Graphite +	0.716	0.26	1.29	0.17		
Graphite -	1.124	0.29	1.55	0.15		
Total	1.90	0.55	2.83	0.32		
CuC-EL +	0.051	1.21	0.092	1.17	0.227	1.72
CuC-EL -	0.085	0.97	0.131	0.16	0.250	1.25
Total	0.136	2.19	0.217	1.33	0.476	2.97
CuC10 +	0.058	1.56	0.082	2.29	0.125	970.*
CuC10 -	0.062	0.79	0.062	1.35	0.115	1200.
Total	0.142	2.35	0.145	3.64	0.245	2170.
AgC62 +	0.561	0.25	0.596	0.49	0.618	122.*
AgC62 -	0.319	0.20	0.356	0.39	0.518	140.
Total	0.879	0.45	0.949	0.87	1.143	262.
AgC10 +	0.054	0.54	0.095	1.49	0.129	2.28
AgC10 -	0.066	0.30	0.053	0.65	0.095	1.65
Total	0.124	0.84	0.149	2.14	0.228	3.93
AgC10H +	0.066	0.38	0.124	0.91	0.213	3.91
AgC10H -	0.046	0.39	0.058	0.56	0.087	1.39
Total	0.111	0.77	0.180	1.47	0.300	5.30
AgC5H +	0.035	1.31	0.059	1.06	0.104	6.20
AgC5H -	0.080	0.93	0.109	0.82	0.088	4.29
Total	0.116	2.24	0.169	1.88	0.192	10.49

\*Run discontinued after 2 hours because of excessive brush wear.

†Total drop measured independently.

Voltage drop measurements were made at intervals throughout each run. The values given in the tables are the averages of all readings recorded. As a check on the volt drop readings at each brush, the total drop across the brush pair was also measured and compared with the sum of the individual drops. Wear measurements were made at approximate 24-hour intervals during the tests. The sum of the periodic wear values was compared with the wear value for the complete run.

Although the usual condition for brushes operating on copper surfaces is with brushes tracking, the tests were made with brushes operat-

Table 2.

Copper Rings: 1850 f.p.m. Brushes Not Tracking  
 Brush Pressure: Graphite 2 P.S.I.  
 All Others 3 P.S.I.

Brush Material and Polarity	60 Amp/Sq In—		120 Amp/Sq In—		400 Amp/Sq In—	
	Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)	Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)	Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)
Graphite +	0.582	0.11	1.25	0.06		
Graphite -	1.365	0.52	1.88	0.11		
Total	1.97	0.63	3.13	0.17		
CuC-EL +	0.038	0.51	0.079	0.39	0.201	1.33
CuC-EL -	0.079	0.29	0.089	0.35	0.187	1.41
Total	0.118	0.80	0.167	0.74	0.389	2.74
CuC10 +	0.070	1.65	0.064	2.01	0.130	4360.*
CuC10 -	0.104	0.64	0.084	1.43	0.150	1280.
Total	0.185	2.29	0.151	3.44	0.280	5640.
AgC62 +	0.306	0.37	0.439	0.37	0.948	27.0 <sup>b</sup>
AgC62 -	0.361	0.34	0.384	0.51	0.504	20.5
Total	0.677	0.71	0.827	0.88	1.525	47.5
AgC10 +	0.035	1.08	0.118	0.98	0.156	2.27
AgC10 -	0.069	0.93	0.122	0.54	0.124	1.20
Total	0.108	2.01	0.239	1.52	0.279	3.47
AgC10H +	0.013	1.10	0.076	1.22	0.222	3.32
AgC10H -	0.143	0.48	0.157	0.51	0.138	1.66
Total	0.160	1.58	0.234	1.73	0.362	4.98
AgC5H +	0.031	0.44	0.029	1.71	0.050	4.63
AgC5H -	0.124	0.70	0.178	1.74	0.174	2.37
Total	0.155	1.14	0.209	2.45	0.223	7.00

\* Run discontinued after  $\frac{1}{2}$  hour because of excessive brush wear.

<sup>b</sup> Run discontinued after 2 hours because of excessive brush wear.

† Total drop measured independently.

ing both ways to determine the effect on voltage drop and wear under the two conditions.

It will be noted that, with one exception, for the runs at 60 amperes per square inch and at 120 amperes per square inch the drop at the positive brush was less with brushes not tracking than with brushes tracking. At 400 amperes per square inch there seemed to be no definite tendency. With but one exception the drop at the negative brush for all current densities was less with brushes tracking. There seemed to be no definite tendency as regards brush wear with respect to brushes tracking and not tracking.

The graphite brushes exhibited a very definite polarity effect. The voltage drop at the positive brush was always less than that at the negative brush. In all cases the wear of the graphite brushes was very low; and, with brushes tracking, the positive and negative graphite brushes wore at approximately the same rate.

The AgC62 brush exhibited greater voltage drop and greater wear at positive polarity than at negative polarity for current densities of both 60 and 120 amperes per square inch. The AgC62 positive and nega-

tive brushes exhibited the least wear of any of the metal-graphite brushes tested, and at 60 amperes per square inch showed less wear than the graphite brushes. The total voltage drop at 60 amperes per square inch was approximately half of that for graphite brushes. At 120 amperes per square inch the total voltage drop was approximately 35 per cent of that for graphite brushes.

The brushes with the higher metal content showed total voltage drops of the order of 5 to 7 per cent of those for graphite brushes. In general, however, they wore several times as rapidly. At 400 amperes per square inch no complete tests of the CuC10 or AgC62 brushes could be made because of the excessive wear. At this high current density the high silver content brushes showed remarkably low voltage drop, only 10 to 15 per cent of that of the graphite brushes operating at 60 amperes per square inch. Although they also exhibited a relatively high rate of wear they were far superior to the corresponding copper brushes in this respect.

The AgC5H brush showed approximately the same volt drop as the AgC10H brush and wore at a faster rate. As a result of the tests on copper and silver rings and of those recorded later on bronze, steel and cast iron rings, it is not believed that the brushes manufactured by the ductile powder process offer any operating advantage over those manufactured by the conventional process.

The CuC-EL brush consisting of 80 per cent copper, 10 per cent lead, 5 per cent tin and 5 per cent carbon showed quite favorable performance both as regards voltage drop and wear. It would be interesting to test a similar brush with silver substituted for copper.

In every case, except for the AgC62 brushes, when using silver-graphite brushes on copper rings, a visible silver film appeared on the brush track beneath the positive brush. The time required for a well-defined film to develop depended upon the value of the brush current densities.

In some cases with silver-graphite brushes operating on separate tracks a light silver film also appeared on the track beneath the negative brush. Apparently the production of the silver film is partly mechanical and partly electrolytic.

### **Voltage Drop and Wear Tests with Silver Rings**

Table 3 lists the results of a series of tests conducted with the two types of 90 per cent silver brushes operating on a pure silver (99.99 per cent) ring at 60, 120 and 400 amperes per square inch, with brushes tracking and not tracking. The volt drops are lower than those recorded in Tables 1 and 2 for the corresponding brushes operating on copper rings under the same conditions. There does not seem to be sufficient consistency as regards wear to permit any conclusions in this respect.

### **Repetitive Tests for Consistency**

Table 4 is included to indicate the consistency obtained with repetitive runs. Because of time and equipment limitations it was not prac-

Table 3.

Silver Rings: 1850 f.p.m. Brush Pressure 3 P.S.I.

Brush Material and Polarity	Brush Arrangement	—60 Amp/Sq In—		—120 Amp/Sq In—		—400 Amp/Sq In—	
		Brush and Contact Drop* (volts)	Brush Wear (in./10,000 hrs)	Brush and Contact Drop* (volts)	Brush Wear (in./10,000 hrs)	Brush and Contact Drop* (volts)	Brush Wear (in./10,000 hrs)
AgC10 +		0.020	0.77	0.031	0.99	0.119	1.59
AgC10 -		0.010	0.69	0.035	0.92	0.112	1.44
Total	Tracking	0.032	1.46	0.066	1.91	0.230	3.03
AgC10 +		0.019	0.93	0.020	2.22	0.091	2.73
AgC10 -	Not	0.021	0.82	0.019	1.73	0.112	1.24
Total	Tracking	0.043	1.75	0.039	3.95	0.203	3.97
AgC10H +		0.010	1.11	0.049	1.05	0.157	2.20
AgC10H -		0.017	1.15	0.035	1.00	0.090	1.76
Total	Tracking	0.028	2.26	0.087	2.05	0.251	3.96
AgC10H +		0.023	1.14	0.100	1.90	0.200	2.85
AgC10H -	Not	0.025	0.81	0.050	0.37	0.085	1.22
Total	Tracking	0.051	1.95	0.154	2.27	0.286	4.07

\*Total drop measured independently.

ticable to take several repeat runs for each test. It is felt that, because of the method of conducting the tests by taking periodic measurements of volt drop and wear and comparing these with final measured values, the results are sufficiently reliable.

Table 4

Copper Rings: 1260 f.p.m. Brushes Tracking

AgC10 Brushes Brush Pressure 3 P.S.I.

Brush Current Density 120 Amperes Per Square Inch

Brush Material and Polarity	Brush and Contact Drop* (volts)	Brush Wear (in./10,000 hrs)	Length of Run (hrs)
AgC10 +	0.143	0.34	
AgC10 -	0.106	0.25	
Total	0.251	0.59	216
AgC10 +	0.135	0.42	
AgC10 -	0.100	0.26	
Total	0.240	0.68	288
AgC10 +	0.139	0.42	
AgC10 -	0.084	0.14	
Total	0.226	0.56	423

\*Total drop measured independently.

### Volt Drop and Wear Tests with Varying Humidity

Table 5 presents data on volt drop and wear obtained in conjunction with the tests of the effect of humidity as illustrated in Figures 1 and 2.

### Effect of Brush Pressure

Table 6 illustrates the effect of change in brush pressure. Since no extensive tests of this type were made, the only conclusion that can be

Table 5.—Effect of Humidity.

Copper Rings: 1260 f.p.m. Brushes not Tracking  
 AgC10 and CuC-EL Brushes Brush Pressure 3 P.S.I.  
 Brush Current Density 400 Amperes per Square Inch

Brush Material and Polarity	Brush and Contact Drop† (volts)	Brush Wear (in./10,000 hrs)	Length of Run (hrs)	Remarks
CuC-EL +	0.199	0.548	135	Run at constant relative humidity of 40%
CuC-EL -	0.127	0.607		
Total	0.332	1.155		Final ring temp. 52 °C.
CuC-EL +	0.264	0.650	168	Run at intermittent high humidity.
CuC-EL -	0.137	0.547		Range between 50 and 100%.
Total	0.399	1.197		Final ring temp. 50 °C.
CuC-EL +	0.222	0.620	168	Run at constant relative humidity of 42% on surface left after run at intermittent high humidity.
CuC-EL -	0.130	0.565		
Total	0.350	1.185		Final ring temp. 47 °C.
AgC10 +	0.123	1.92	135	Run at constant relative humidity of 40%.
AgC10 -	0.124	1.17		
Total	0.251	3.09		Final ring temp. 42 °C.
AgC10 +	0.112	1.05	168	Run at intermittent high humidity*
AgC10 -	0.151	1.25		Range between 50 and 100%.
Total	0.267	2.30		Final ring temp. 42 °C.
AgC10 +	0.114	2.32*	168	Run at constant relative humidity of 42% on surface left after run at intermittent high humidity.
AgC10 -	0.118	1.27		
Total	0.236	3.59		Final ring temp. 40 °C.

\*Excessive wear occurred during last 48 hours of run simultaneously with appearance of a spotted silver surface on the track under the positive silver brush.

†Total drop measured independently.

drawn is that brush pressure appears to have an effect on both volt drop and wear. Further investigation of the effects of brush pressure seems warranted.

Table 6.—Effect of Brush Pressure.

Copper Rings: 1850 f.p.m. Brushes Tracking  
 Brush Current Density 400 Amperes per Square Inch.

Brush Material and Polarity	Brush Pressure (lbs/sq in.)	Brush Contact Drop* (volts)	Brush Wear (in./10,000 hrs)	Length of Run (hrs)
AgC10 +	2	0.205	22.5	106
AgC10 -		0.077	5.6	
Total		0.285	28.1	
AgC10 +	3	0.129	2.28	105
AgC10 -		0.095	1.65	
Total		0.228	3.93	
AgC10 +	4	0.103	4.82	106
AgC10 -		0.059	3.47	
Total		0.173	8.29	

\*Total drop measured independently.



TESTS OF METAL-GRAPHITE BRUSHES ON BRONZE, STEEL AND  
CAST IRON SLIP RINGS

## Description of Tests

As a basis of comparison for the metal-graphite brushes operating on bronze, steel and cast-iron rings, the General Electric Company's Type H brush was used. It is of electrographitic carbon and is recommended for operation on slip rings at a current density of 55 amperes per square inch, at speeds above 3000 f.p.m.

One grade of copper-graphite brush consisting of 75 per cent copper and 25 per cent graphite was tested. It is designated as CuC25 in the tables.

The silver-graphite brushes tested can be divided into two classifications according to their method of manufacture. Those designated as AgC40, AgC25 and AgC10 were all supplied by the same manufacturer and were made by the conventional method. The brushes designated as AgC12H, AgC10H, AgC5H and AgC3H were supplied by a different manufacturer. They were produced by a new method called the ductile powder process. In each designation the figures represent the percentage of graphite present in the brush.

The slip rings on which all of these brushes were tested at different current densities and ring speeds were of bronze alloy, steel and cast iron.

For this particular series of tests direct current was used. The comparisons, therefore, apply particularly to the use of the various brushes on the field rings of alternators.

In each case the tests made were of sufficient duration to give a reasonable amount of wear. Periodic measurements of wear were made throughout the tests. In cases where the periodic measurements indicated a high rate of wear the tests were correspondingly shortened.

During the earlier tests of the series, brush wear was determined both by micrometer measurement and by measurement of the loss in weight. For later tests the loss of weight method was discarded because of the time it consumed and because it was felt that the micrometer method was sufficiently accurate.

To obviate any differences in wear characteristics caused by variations of pressure on different brushes (due to variations in brush springs, brush length, etc.) the brush holders were modified so that the pressure on the individual brushes could be very accurately adjusted. At the beginning of each run all collector rings were carefully cleaned and smoothed to eliminate any inconsistencies in wear caused by variation in ring surface. Preliminary to the actual run all brushes were carefully fitted to the ring surfaces. At short intervals throughout the tests voltage drop measurements were taken. The tabulated values represent the average of a large number of measurements. To check the voltage drop measurements the total drop across a pair of brushes was measured and compared with the sum of the individual drops. The current was held

approximately constant and was continuously recorded by a recording ammeter.

The tests were conducted in room atmosphere. The temperature variation in the room was never more than 5 °C. The maximum variation in relative humidity was about 34 per cent. However, for any given series in the group the variation did not usually exceed 10 per cent.

At the conclusion of each run the ring surface temperature was measured by mercury thermometers held at the ring surface with putty.

The tests were conducted at ring surface speeds of approximately 2500 f.p.m. and 3600 f.p.m. and at brush current densities of 75 amperes per square inch and 150 amperes per square inch.

### Discussion of Results

Tables 7, 8 and 9 list data obtained in testing the various types of brushes on bronze, steel and cast-iron rings at brush current densities

Table 7.

Bronze Rings: 2500 f.p.m. Brushes not Tracking Brush Pressure 2 P.S.I.						
Brush Material and Polarity	75 Amp/Sq In Brush Wear (in./10,000 hrs)			Ring Temp. Rise (°C)	150 Amp/Sq In Brush Wear (in./10,000 hrs)	
	Drop (volts)*				Drop (volts)*	Ring Temp. Rise (°C)
Graphite +	1.20	0.17	22.7	1.22	0.28	37.7
Graphite -	1.21	3.38	21.2	1.73	10.94	47.3
Total	2.42	3.55		2.95	11.22	
CuC25 +	0.339	1.43	15.4	0.431	3.01	19.2
CuC25 -	0.288	1.74	16.3	0.413	1.83	25.6
Total	0.633	3.17		0.845	4.84	
AgC40 +	0.524	0.15	12.1	0.634	0.32	17.8
AgC40 -	0.378	0.27	10.7	0.464	0.35	15.6
Total	0.902	0.42		1.098	0.67	
AgC25 +	0.242	0.64	11.2	0.292	2.48	13.0
AgC25 -	0.260	0.33	13.4	0.498	1.66	16.3
Total	0.513	0.97		0.800	4.14	
AgC10 +	0.065	2.47	9.5	0.115	3.96	13.0
AgC10 -	0.118	0.74	12.2	0.199	0.90	15.4
Total	0.183	3.21		0.314	4.86	
AgC12H +	0.199	0.46	10.9	0.235	0.80	12.8
AgC12H -	0.231	0.37	13.9	0.224	1.06	16.5
Total	0.420	0.83		0.459	1.86	
AgC10H +	0.136	0.42	11.3	0.348	3.42	16.4
AgC10H -	0.230	0.60	11.1	0.238	0.74	14.3
Total	0.365	1.02		0.582	4.16	
AgC5H +	0.069	0.48	12.0	0.172	1.57	11.8
AgC5H -	0.098	0.59	14.5	0.207	0.63	13.5
Total	0.172	1.07		0.375	2.20	
AgC3H +	0.085	0.34	7.9	0.168	2.57	11.5
AgC3H -	0.143	1.05	9.3	0.163	1.21	11.6
Total	0.230	1.39		0.321	3.78	

\*Total drop measured independently.

Table 8.

Steel Rings: 2500 f.p.m. Brushes Not Tracking  
Brush Pressure 2 P.S.I.

Brush Material and Polarity	75 Amp/Sq In			150 Amp/Sq In		
	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)
Graphite +	1.68	1.94	25.2	2.02	3.30	55.2
Graphite -	2.19	4.96	25.0	2.93	9.90	59.3
Total	4.04	6.90		4.97	13.20	
CuC25 +	0.335	1.00	11.8	0.496	2.19	18.3
CuC25 -	0.570	1.23	15.2	0.659	2.92	17.3
Total	0.911	2.23		1.172	5.11	
AgC40 +	0.583	0.14	12.4	0.731	1.35	17.8
AgC40 -	0.872	0.24	13.5	0.825	0.89	18.2
Total	1.455	0.38		1.556	2.24	
AgC25 +	0.288	0.56	12.1	0.362	1.54	24.2
AgC25 -	0.355	1.06	12.9	0.284	3.10	15.4
Total	0.656	1.62		0.652	4.64	
AgC10 +	0.126	2.12	7.4	0.135	1.46	9.8
AgC10 -	0.319	2.33	9.8	0.303	7.98	10.4
Total	0.445	4.45		0.438	9.44	
AgC12H +	0.284	0.74	12.5	0.326	17.1	17.8
AgC12H -	0.584	11.36	13.1	0.631	23.8	14.8
Total	0.869	12.10		0.952	40.9	
AgC10H +	0.133	0.92	10.7	0.622	17.5	21.4
AgC10H -	0.552	12.75	13.3	0.615	33.8	21.0
Total	0.685	13.67		1.235	51.3	
AgC5H +	0.178	0.79	9.5	0.119	1.48	12.5
AgC5H -	0.528	9.86	14.4	0.353	12.8	12.8
Total	0.707	10.65		0.473	14.28	
AgC3H +	0.155	1.64	8.1	0.111	4.44	7.8
AgC3H -	0.260	4.85	9.4	0.181	54.3	15.0
Total	0.417	6.49		0.309	58.74	

\*Total drop measured independently.

of 75 amperes per square inch and 150 amperes per square inch for peripheral ring speeds of 2500 feet per minute.

Table 10 lists the data for the same brushes on the same rings when operating with a peripheral speed of 3680 feet per minute and at a brush current density of 75 amperes per square inch. The tests for the brushes operating at 150 amperes per square inch with peripheral ring speeds of 3680 feet per minute are now in progress. The tests will not be completed in time to include the test data in this report.

It will be noted that in every case the voltage drop across the positive graphite brush and contact was less than that across the negative graphite brush and contact. In every case also the wear of the positive brush was less than that of the negative brush.

No such consistency is apparent in the case of the metal-graphite brushes. In most cases the drop at the positive brush was less than that at the negative brush, but in several cases the effect was reversed.

Table 9.

Cast-iron Rings: 2500 f.p.m. Brushes not Tracking  
Brush Pressure 2 P.S.I.

Brush Material and Polarity	75 Amp/Sq In			150 Amp/Sq In		
	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)
Graphite +	1.74	0.60	24.6	1.83	1.30	53.6
Graphite -	2.61	5.41	28.0	2.72	9.15	67.0
Total	4.40	6.01		4.56	10.45	
CuC25 +	0.354	0.88	13.3	0.526	2.55	22.0
CuC25 -	0.517	1.05	16.4	0.738	6.21	30.8
Total	0.911	1.93		1.276	8.76	
AgC40 +	0.703	0.18	13.0	1.039	9.45	22.8
AgC40 -	0.832	0.42	14.5	0.807	1.75	18.3
Total	1.535	0.60		1.846	11.20	
AgC25 +	0.311	0.94	11.6	0.337	2.27	15.4
AgC25 -	0.402	0.96	12.4	0.443	2.80	16.0
Total	0.721	1.90		0.781	5.07	
AgC10 +	0.135	4.25	9.1	0.195	3.90	11.8
AgC10 -	0.395	3.34	13.4	0.396	7.00	14.8
Total	0.530	7.59		0.591	10.90	
AgC12H +	0.210	1.49	11.8	0.644	24.4	23.7
AgC12H -	0.798	10.20	16.7	0.790	29.3	22.8
Total	1.010	11.69		1.437	53.7	
AgC10H +	0.121	0.42	10.8	0.372	5.31	13.9
AgC10H -	0.686	9.61	14.6	0.704	24.5	23.5
Total	0.810	10.03		1.080	30.71	
AgC5H +	0.143	0.51	9.9	0.218	1.83	12.4
AgC5H -	0.416	4.02	12.1	0.521	13.4	19.7
Total	0.558	4.53		0.745	15.23	
AgC3H +	0.205	1.00	7.0	0.188	0.42	10.2
AgC3H -	0.369	8.11	10.1	0.178	5.02	12.2
Total	0.559	9.11		0.367	5.44	

\*Total drop measured independently.

The inconsistency is even more apparent with respect to wear. According to the theory of electrolytic action, the positive brush would be expected to exhibit the greater wear since the current is from brush to ring. However, it will be noted that, although in a few cases the positive brush did show greater wear, in a majority of cases the negative brushes exhibited greater wear.

The brushes made by the ductile powder process showed particularly high wear when operating at negative polarity on steel and cast-iron rings.

The results do not indicate any particular relationship between brush wear and ring temperature rise. For example, in the case of the AgC10H brushes operating at 150 amperes per square inch on steel rings at 2500 f.p.m., the voltage drops at positive and negative brushes are approximately equal, and the negative brush shows practically double the wear of the positive brush. Yet the temperature rises at the surfaces of the positive and negative rings are approximately equal. Or, in the case of

Table 10.—Slip Ring Operation at 3680 f.p.m.

Brush Pressure 2 P.S.I.  
 Brushes on Separate Tracks.  
 Current Density 75 amp/sq in

Brush Material and Polarity	Bronze Rings 75 Amp/Sq In			Steel Rings 75 Amp/Sq In			Cast-iron Rings 75 Amp/Sq In		
	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)	Drop (volts)*	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)
Graphite +	1.55	0.15	14.5	1.53	0.46	21.3	1.57	0.83	21.0
Graphite -	1.98	6.37	22.3	2.49	5.50	24.6	2.79	5.12	28.3
Total	3.53	6.52		4.03	5.96		4.36	5.95	
CuC25 +	0.356	1.92	8.5	0.364	2.29	10.0	0.560	1.55	11.0
CuC25 -	0.420	2.25	12.3	0.693	5.26	10.3	0.751	1.98	12.4
Total	0.776	4.17		1.060	7.55		1.316	3.53	
AgC40 +	0.826	0.19	11.3	0.593	0.71	11.7	0.749	1.06	11.0
AgC40 -	0.732	1.03	11.8	0.930	0.06	12.2	0.936	0.92	11.7
Total	1.564	1.22		1.518	0.77		1.710	1.98	
AgC25 +	0.759	0.23	10.2	0.251	1.91	10.0	0.354	1.21	9.7
AgC25 -	0.305	0.47	13.4	0.537	1.23	9.1	0.565	1.85	11.6
Total	1.062	0.70		0.788	3.14		0.921	3.06	
AhC10 +	0.049	3.88	7.1	0.069	7.18	8.0	0.121	6.56	7.8
AhC10 -	0.138	2.07	8.3	0.185	10.6	7.9	0.332	3.90	9.1
Total	0.187	5.95		0.265	17.78		0.453	10.46	
AgC12H +	0.080	0.71	14.8	0.118	2.03	10.5	0.064	2.4	9.4
AgC12H -	0.151	1.26	14.9	0.610	18.9	11.7	0.763	10.3	14.8
Total	0.231	1.97		0.729	20.93		0.830	12.7	
AgC10H +	0.235	17.4	11.0	0.074	1.35	9.7	0.107	1.39	9.0
AgC10H -	0.160	1.08	16.5	0.633	16.2	11.2	0.728	12.7	13.7
Total	0.395	18.48		0.711	17.55		0.835	14.09	
AgC5H +	0.061	0.61	7.0	0.181	2.11	11.1	0.196	1.32	9.0
AgC5H -	0.162	0.21	8.4	0.493	10.2	13.5	0.376	23.2	8.0
Total	0.228	0.82		0.676	12.31		0.575	24.52	
AgC3H +	0.059	0.60	7.9	0.226	8.40	9.9	0.186	7.01	7.9
AgC3H -	0.155	55.1	7.7	0.360	9.75	9.0	0.406	7.75	10.9
Total	0.214	55.70		0.572	18.15		0.594	14.76	

\*Total drop measured independently.

the AgC5H brushes operating under the same conditions on the same rings, the voltage drop at the negative brush is almost exactly three times that at the positive brush, and the wear of the negative brush is more than eight times that of the positive brush. Yet the temperatures at the positive and negative ring surfaces are almost identical. These results would indicate that high brush wear is not necessarily coupled with high friction loss. While it is true that all the rings were connected in series in the same electrical circuit and were, therefore, connected together by good electrical and thermal conductors, it is also true that the ring surfaces under the graphite brushes exhibited much higher temperature rises than the ring surfaces operating simultaneously in the same circuit under silver-graphite brushes. It is, therefore, not believed that the thermal characteristics of the circuit can account for the discrepancies between ring surface temperature rise and brush wear.

One very striking thing about the results is the very favorable wear characteristics shown by the AgC40 brush operating at either polarity. With but one exception, where the wear characteristics of the positive AgC40 brush seemed totally inconsistent, the positive AgC40 brush showed greater life at both speeds than any of the other metal-graphite brushes. With but one other exception this brush showed greater life than the graphite brush at 2500 f.p.m. The negative AgC40 brush showed longer life than the graphite brush under all conditions, and with one exception longer life than any of the other metal-graphite brushes.

Bronze rings showed what appeared to be a silver film on the brush track when operating with any of the silver-graphite brushes except the AgC40.

In the case of the steel and cast-iron rings it was difficult to determine whether a silver film was present because of the similarity in color between the ring metal and the silver.

The results obtained are of challenging interest and invite further investigation. However, the immediate problem is to determine, on the basis of results at hand, whether silver can be economically used as a component of brushes.

Costs of manufacturing silver-graphite brushes on the same commercial scale as graphite or copper graphite brushes are not available. It should be pointed out that only that portion of the brush which constitutes wearing surface need be of the silver-graphite mix. The upper part of the brush can be of copper-graphite, in order to save on silver cost and decrease the initial cost of the brush.

### Economic Comparisons

It is possible to develop an equation for the price one could afford to pay for one brush as compared with another to give the same total cost, *viz.*:

Let  $x$  = the price in dollars of the brush taken as the standard of comparison;

$y$  = the price in dollars of the brush to be compared;

$a$  = the fraction of the standard brush used up per 10,000 hours;

$b$  = the fraction of the compared brush used up per 10,000 hours;

$I$  = the current flowing in the series circuit of the two brush types;

$E_x$  = the voltage drop across the standard brush and sliding contact;

$E_y$  = the voltage drop across the compared brush and sliding contact;

$F_x$  = the friction loss of the standard brush in kwh. per 10,000 hours;

$F_y$  = the friction loss of the compared brush in kwh. per 10,000 hours;

$C$  = the cost of energy in dollars per kilowatt hour;

$R$  = the fixed charge rate on brushes.

Assume continuous operation.

(1) Then the cost of the standard brush per 10,000 hours is

$$ax + \frac{10,000}{8760} Rx + \frac{10,000}{1000} E_x IC + F_x C$$

(2) and the cost of the compared brush per 10,000 hours is

$$by + \frac{10,000}{8760} Ry + \frac{10,000}{1000} E_y IC + F_y C$$

For equal cost (1) = (2)

$$by + \frac{10,000}{8760} Ry + \frac{10,000}{1000} E_y IC + F_y C =$$

$$ax + \frac{10,000}{8760} Rx + \frac{10,000}{1000} E_x IC + F_x C$$

$$\text{Then } \left( b + \frac{10,000R}{8760} \right) y = \left( a + \frac{10,000R}{8760} \right) x + 10IC(E_x - E_y) + C(F_x - F_y)$$

$$\text{and } y = \left( \frac{a + 1.14R}{b + 1.14R} \right) x + \frac{10IC(E_x - E_y)}{b + 1.14R} + \frac{C(F_x - F_y)}{b + 1.14R}$$

If two standard brushes are used in parallel to one of the compared type, that is, if the compared brush is to be operated at twice the current density of the standard brush, then

$$y = \left( \frac{a + 1.14R}{b + 1.14R} \right) 2x + \frac{10IC(E_x - E_y)}{b + 1.14R} + \frac{C(2F_x - F_y)}{b + 1.14R}$$

In this particular case, since no friction loss measurements have yet been made, the comparison between the various types of brushes has been based on the same friction loss with all brushes regardless of method of operation, that is, the term involving the friction loss has been neglected. Examination of the equation will show that if  $F_x$  is greater than  $F_y$  the value of  $y$  will be increased. It will also be apparent that, in the case where a single compared brush replaces two standard brushes, the value of  $y$  is increased, not only because of the doubling of the value of the first term of the equation, but because in the last term of the equation the difference in friction loss becomes the difference between the friction loss of two standard brushes and one compared brush.

Assuming the friction losses to be the same for both types of brushes, the equations then become

$$y = \left( \frac{a + 1.14R}{b + 1.14R} \right) x + \frac{10IC(E_x - E_y)}{b + 1.14R}$$

for both brushes operating at the same current density,

$$\text{and } y = \left( \frac{a + 1.14R}{b + 1.14R} \right) 2x + \frac{10IC(E_x - E_y)}{b + 1.14R}$$

for the compared brush operating at twice the current density for the standard brush.

For comparative purposes the graphite brush operating at the same polarity as the compared brush has been taken as standard.

Fixed charges have been taken at 10 per cent per annum.

Energy cost has been assumed to be  $\frac{1}{2}$  cent per kilowatt hour.

The useful wear of the brushes considered is assumed to be 1 inch (approximately 50 per cent of overall length).

The price of the graphite brush considered as standard (Electrographitic,  $1\frac{1}{4}'' \times \frac{3}{4}'' \times 2\frac{3}{8}''$ ) is \$0.877 per brush. Then for both brushes operating at 75 amperes per square inch

$$y = \left( \frac{a + 0.114}{b + 0.114} \right) x + \frac{\$3.75(E_x - E_y)}{b + 0.114},$$

and for the graphite brush at 75 amperes per square inch and the compared brush at 150 amperes per square inch

$$y = \left( \frac{a + 0.114}{b + 0.114} \right) 2x + \frac{\$7.50(E_x - E_y)}{b + 0.114}$$

As an illustration, comparing the positive AgC40 brush with the positive graphite brush both operating at 75 amperes per square inch on bronze rings with a brush pressure of 2 pounds per square inch, (Table 7):

$$\begin{aligned} y &= \left( \frac{0.17 + 0.114}{0.15 + 0.114} \right) x + \frac{\$3.75(1.20 - 0.524)}{0.15 + 0.114} \\ &= \left( \frac{0.284}{0.264} \right) x + \frac{\$3.75 \times 0.676}{0.264} \\ &= 1.07x + \$9.61 \\ &= 1.07(\$0.877) + \$9.61 \\ &= \$0.94 + \$9.61 = \$10.55 \end{aligned}$$

In other words, assuming the friction losses equal, one could afford to pay \$10.55 for the positive AgC40 brush to give the same total cost as for the graphite brush.

If the AgC40 brush can be purchased for a price less than \$10.55 the AgC40 brush will show a saving over the graphite brush used under the specified conditions.

Tables 11, 12 and 13 list the values of  $y$ , calculated in a manner similar to the example cited, for the silver-graphite and copper-graphite



brushes all manufactured by the conventional powder process. From an inspection of the wear rates indicated in Table 7, 8, 9 and 10 for the

Table 11.

Assumptions:

Cost of Graphite Brush = \$0.877  
 Cost of Energy =  $\frac{3}{4}$ ¢ per kwh.  
 Fixed Charge Rate = 10%  
 Continuous Operation  
 Friction Loss Same for all Brushes

Type of Brush	Current Density (Amp/Sq In)	-2500 f.p.m.-		-3680 f.p.m.-	
		Pos.	Neg. Equivalent Price of Brush*	Pos.	Neg.
AgC40	75	\$10.55	\$16.10	\$9.70	\$ 9.05
AgC40	150	\$10.92	\$25.30		
AgC25	75	\$ 5.10	\$14.99	\$9.29	\$20.53
AgC25	150	\$ 2.81	\$10.72		
AgC10	75	\$ 1.75	\$ 8.40	\$1.47	\$ 5.78
AgC10	150	\$ 2.12	\$13.55		
CuC25	75	\$ 2.25	\$ 3.54	\$2.31	\$ 4.99
CuC25	150	\$ 2.00	\$ 6.23		

\*Equivalent price of brush represents what one could pay for the brush considered to give the same total cost of operation as for the graphite brush at the assumed price. Any price less than that tabulated would give a saving in favor of the brush considered.

brushes manufactured by the ductile powder process, it is evident that in general these brushes could not compete with the brushes manufactured by the conventional process. They have, therefore, not been included in the tables of equivalent prices.

It will be noted that the most economical solution need not be to use both positive and negative brushes of the same material, nor at the same current density.

Table 12.—Steel Rings.

Assumptions: Cost of Graphite Brush = \$0.877

Cost of Energy =  $\frac{3}{4}$ ¢ per kwh

Fixed Charge Rate = 10%

Continuous Operation

Friction Loss Same for All Brushes

Type of Brush	Current Density (Amp/Sq In)	-2500 f.p.m.-		-3680 f.p.m.-	
		Pos.	Neg. Equivalent Price of Brush*	Pos.	Neg.
AgC40	75	\$23.28	\$26.45	\$4.87	\$61.80
AgC40	150	\$ 7.33	\$21.17		
AgC25	75	\$10.42	\$ 9.85	\$2.50	\$ 9.09
AgC25	150	\$ 8.15	\$ 7.22		
AgC10	75	\$ 3.27	\$ 4.99	\$0.82	\$ 1.26
AgC10	150	\$ 9.63	\$ 2.84		
CuC25	75	\$ 6.14	\$ 7.81	\$2.03	\$ 2.16
CuC25	150	\$ 5.40	\$ 6.73		

\*Equivalent price of brush represents what one could pay for the brush considered to give the same total cost of operation as for the graphite brush at the assumed price. Any price less than that tabulated would give a saving in favor of the brush considered.

In any case, the highest price indicated in the tables for a brush of a given classification indicates the most economical solution and the brush should, therefore, be operated under the conditions tabulated to give best economy.

To illustrate the use of the tables let us assume that we wish to determine the most economical brush to use on bronze rings operating at 2500 f.p.m.

Table 13.—Cast-iron Rings

Assumptions: Cost of Graphite Brush = \$0.877  
 Cost of Energy =  $\frac{1}{2}$ ¢ per kwh  
 Fixed Charge Rate = 10%  
 Continuous Operation  
 Friction Loss Same for All Brushes.

Type of Brush	Current Density (Amp/Sq In)	-2500 f.p.m.		-3680 f.p.m.-	
		Pos.	Neg.	Pos.	Neg.
AgC40	75	\$15.35	\$21.57	\$3.32	\$11.14
AgC40	150	\$ 5.62	\$12.47		
AgC25	75	\$ 5.67	\$12.20	\$4.07	\$ 6.59
AgC25	150	\$ 4.92	\$ 8.93		
AgC10	75	\$ 1.52	\$ 3.80	\$0.94	\$ 3.44
AgC10	150	\$ 3.19	\$ 3.80		
CuC25	75	\$ 6.30	\$20.07	\$2.77	\$ 5.85
CuC25	150	\$ 3.89	\$ 3.89		

\*Equivalent price of brush represents what one could pay for the brush considered to give the same total cost of operation as for the graphite brush at the assumed price. Any price less than that tabulated would give a saving in favor of the brush considered.

In the first place Table 11 indicates that the most economical silver-graphite brush to use in this case is the AgC40 brush operated at 150 amperes per square inch. For the same total cost as the graphite brush one could afford to pay \$10.92 for the AgC40 brush in the positive position and \$25.30 for the AgC40 brush in the negative position. Similarly, considering the CuC25 brush, the most economical condition is to use the positive CuC25 brush at 75 amperes per square inch and the negative CuC25 brush at 150 amperes per square inch, that is, twice as many positive CuC25 brushes as negative CuC25 brushes.

We can also say that for positive polarity the CuC25 brush at 75 amperes per square inch selling at \$2.25 will give the same total cost as the AgC40 brush at 150 amperes per square inch selling at \$10.92.

The present commercial price of the CuC25 brush tested is approximately \$1.46.

The tables indicate that, in most cases for the test conditions obtaining, the AgC40 brush was the best of the silver brushes.

### Effect of Friction Loss

It should again be emphasized that all these comparisons are based on the same friction loss for all brushes, because of lack of present infor-

mation on the friction loss. However, examination of the catalogs of several brush manufacturers indicates that in general the coefficients of friction of commercial copper-graphite brushes are less than for electro-graphitic carbon brushes. If this is also true for the silver-graphite brushes the cost comparisons between electrographitic and silver-graphite brushes would be even more favorable for the latter.

### Other Considerations

It is understood by the authors that copper-graphite brushes are seldom used on steel or cast-iron slip rings because of the tendencies of these brushes to score the rings. No such tendency was apparent with silver-graphite brushes during the tests reported here, and this factor might be an important consideration in comparing copper-graphite and silver-graphite brushes.

It might also be pointed out that in cases where a single metal-graphite brush at double density can be substituted for a graphite or other brush at single density the number of brush holders can be reduced. Other factors entering into the comparison are brush maintenance and brush fitting when brush replacements are necessary and possibly less tendency for selective action if brushes operate in parallel.

### Effect of Brush Pressure

Table 14 lists the results of preliminary tests to determine the effect of increase in brush pressure on volt drop and brush wear. For these preliminary tests the brushes chosen were the AgC12H and AgC10H manufactured by the ductile powder process, because they had shown

Table 14.—Effect of Brush Pressure.

Steel Rings: 2500 f.p.m. Brushes not Tracking  
Brush Current Density 150 Amp/Sq In  
Room Temperature 25 °C Relative Humidity 57%

Brush Material and Polarity	Brush Pressure = 2 P.S.I.—			Brush Pressure = 3 P.S.I.—		
	Drop (volts)	Brush Wear (in./10,000 hrs)	Ring Temp. Rise (°C)	Drop (volts)	Brush Wear (in./10,000 hrs)	Ring Temp. Ri (°C)
AgC12H +	0.326	17.1	17.8	0.060	1.04	15.2
AgC12H -	0.631	23.8	14.8	0.648	33.0	14.8
Total	0.952	40.9		0.710	34.0	
AgC10H +	0.622	17.5	21.4	0.506	3.40	16.5
AgC10H -	0.615	33.8	21.0	0.540	29.6	17.6
Total	1.235	51.3		1.056	33.0	

particularly severe wear at two pounds per square inch. It will be noted that increased brush pressure gave lower voltage drops and wear rates in every case except for the negative AgC12H brush. The improvement in wear characteristics was particularly significant in the case of positive brushes of both types. The tests indicate that further investigation of the effects of brush pressure should be made.

### Tests at Higher Speed

A short series of tests was run on steel rings operating at peripheral speeds of approximately 10,000 feet per minute. To obtain this speed with the 19-inch diameter steel rings available, it was necessary to rotate the rings at approximately 2000 r.p.m. At this speed difficulty was experienced with vibration of the brush rigging. For this reason it is not felt that the data obtained was indicative, and it is, therefore, not presented. The equipment will be redesigned to eliminate the vibration, and further tests will be made.

### CONSIDERATIONS IN THE USE OF THE METAL-GRAPHITE BRUSH

In the operation of sliding contacts with rotating copper surfaces the copper oxide film formed in ordinary atmospheres seems to have an important bearing on the contact voltage drop.

It is believed by the authors that at least a part of the lowered contact drop when using brushes of high copper content may be due to the abrasive action of the brushes, which removes the oxide film. A brush which is sufficiently abrasive to remove the oxide film must also have an abrasive action on the rotating metal surface and must cause more rapid wear of that surface.

If the copper surface is given a coating of silver, the contaminating film which forms is usually silver sulfide which is a far better conductor than copper oxide.

All the tests conducted have definitely indicated the establishment of a silver film on the positive brush track of both copper and bronze rings when operating with high silver content silver-graphite brushes. In some of the tests a lighter silver film was also visible on the negative brush track. In the cases of the steel and cast-iron rings, because of the similarity of the colors of the brush and ring materials, it was not possible to distinguish visibly whether a silver film was present. However, the low voltage drop indicates a better contact than that between graphite brushes and rings and it is, therefore, believed that a silver film is present on these rings also.

Regardless of whether the better contact between brush and ring is accomplished by removal of the copper oxide film with copper-graphite brushes or by the establishment of a more desirable film with silver-graphite brushes, the metal-graphite brushes show low contact voltage drop and, therefore, low electrical loss at the contact. The advantage is twofold: first, an increase in electrical efficiency, and second a decrease in local heating due to electrical loss.

No comparative measurements of friction loss have yet been made. However, on the basis of ring temperature measurements made during the tests and of information obtained from brush manufacturers' catalogs on the relative friction coefficients of graphite and metal-graphite brushes,

it is believed that the metal-graphite brushes may also show substantial savings in this respect.

The chief obstacle which the silver-graphite brush has to overcome in order to prove economical is its higher initial cost. While the authors are not in a position to speculate about what the price of the silver brush would be if manufactured on a commercial scale, they believe that the cost ratio would not be as great as the ratio of the costs of the component materials. The manufacturing process cost constitutes a considerable part of the total cost of the usual brush. The silver-graphite brush is manufactured by the same process as that used for the copper-graphite brush. It is expected that the manufacturing costs would be approximately the same for both brushes. The total cost of either brush would be the processing cost plus the cost of materials. The ratio of total costs would, therefore, include the processing costs and would not be in the proportion of material costs alone.

For one brush to prove more economical than some other brush taken as a standard of comparison, the saving in electrical and friction losses must more than offset any increase in wear cost and fixed charges. Other factors may also enter into the problem. For example, if fewer of the compared brushes need be used (as would be the case if a higher current density were used) fewer brush holders would be required. Additional savings may result because of decreased labor charges for brush fitting and maintenance, and because of a shorter outage period for the machine to which the brushes are fitted.

In the design of commutator machines it might be possible to shorten the commutator and thus decrease the cost of the machine.

### Conclusions

As a result of the tests so far conducted the following conclusions have been drawn:

1. A silver film is established on the brush track under high silver content silver-graphite brushes when operating at positive polarity.
2. A silver film is established in some cases under high silver content silver-graphite brushes when operating at negative polarity.
3. The establishment of the silver film seems to depend on both current density and brush pressure.
4. The brush contact drop is very low for high silver content silver-graphite brushes.
5. Humidity variation affects the contact drop of both silver-graphite and copper-graphite brushes. The proportionate effect is less in the case of the silver-graphite brushes.
6. Silver-graphite brushes manufactured by the ductile powder process are in general less satisfactory from the viewpoint of wear than those manufactured by the conventional process.

7. The AgC40 brush, particularly when operating on steel and cast-iron slip rings, is in general more economical than the graphite brush.
8. Brushes containing more than 90 per cent of silver do not seem practical for operation on copper surfaces because of excessive brush wear.
9. Brushes containing more than 75 per cent of silver do not seem practical for operation on steel and cast-iron slip rings.
10. Silver-graphite brushes do not score steel and cast-iron slip rings at speeds at which scoring is caused by copper-graphite brushes.
11. In some cases the most economical solution of the brush-slip ring problem is to use brushes of different compositions on positive and negative slip rings.
12. In some cases the use of different brush current densities on positive and negative slip rings is warranted.

#### FUTURE INVESTIGATION

##### Slip Ring Operation with Direct Current

Because of the inconsistencies indicated in the tabulation of run data, particularly as regards wear, it is felt that considerably more investigation should be carried on with slip rings operating with direct current. Some of the tests which seem warranted are:

Further investigation of the effects of brush pressure.

Further investigation of the effects of humidity.

Investigation of the effects of atmospheres containing such common contaminants as sulfur and ammonia.

Tests at higher ring speeds.

Tests of other compositions of copper-graphite and silver-graphite brushes.

All these are on the test program but have been carried out only to a very limited extent because of lack of time.

Since tests involving wear measurements require runs of comparatively long duration such a program must necessarily extend over a considerable time.

##### Commutator Operation on Direct Current Machinery

Although to date this phase of the investigation has not been pursued to any extent, the results obtained with copper slip rings and direct current indicate good possibilities. The authors do not believe that with modern interpole machines high-resistance brushes are necessary for satisfactory commutation. The only actual test on commutators in this investigation is now in progress. A 14-volt D.C. generator used for filament supply for a local radio station has been equipped with silver-graphite brushes. With the original carbon brushes the characteristics of the circuit were such that the generator would barely supply the

required current when operating at full field. Silver-graphite brushes of 90 per cent silver content were substituted for the original carbon brushes. A net gain of approximately 2 volts was obtained so that the generator now easily supplies the circuit. The commutator has developed a pronounced polished silver surface on the brush track and commutation is perfect. At the time this was written the machine had not been in operation for a sufficiently long period to give reliable brush wear indications. Further investigation of this field seems warranted.

### **Slip Ring Operation with Alternating Current**

Up to the time this was written no investigation of the use of silver-graphite brushes on slip rings with alternating current had been conducted. Since the silver plating of the rings by the brushes seems to be partly mechanical and partly due to current flow, it appears that this field should also be investigated. Low contact loss, if coupled with reasonable brush wear, would be highly desirable.

## Chapter 14

### Silver as a Catalyst

BY ALLAN R. DAY \* AND TONY IMMEDIATA †

#### INTRODUCTION

It has long been known that the presence of a relatively small amount of an extraneous substance may greatly influence chemical action between two or more given compounds. Usually a catalyst is defined as a substance which, in minimal amounts, will bring about the transformation of large quantities of the reactants and which will be unchanged in its chemical composition at the end of the reaction. The physical state of the catalyst, however, frequently becomes greatly altered during the reaction. In general a catalyst is supposed to accelerate the reaction to the same degree in both directions and hence does not modify the final state of equilibrium.

The majority of catalytic reactions are of the heterogeneous type, that is the catalyst and the substrate are found in two different phases. A large number of these are gaseous reactions, occurring at solid surfaces. In the latter type the surface of the solid catalyst is the source of catalytic activity and adsorption on the surface appears to be essential for occurrence of the catalytic action. This would indicate a definite relationship between the particle size of the catalyst and its activity, and in many cases it has been shown that the finer the division of the catalyst the greater the activity of the mass. In other words the adsorption capacity for a given catalyst is determined to some extent by the area of the exposed surface. Sintering effects on the surface often prevent taking full advantage of this relationship between particle size and activity. Frequently, far below the melting point, a finely divided powder will pack together through surface fusion, or recrystallization of small crystals at the surface may yield larger ones. In either case the result is the same, namely the reduction of surface area and decrease in activity. The form of the catalyst employed is an important factor in any consideration of catalyst efficiency.

Catalysts may be used in pellet or granular form. In other cases they are used on carriers. The term carrier usually refers to a porous material such as pumice, asbestos, unglazed porcelain or charcoal, which when impregnated with the catalyst offers a larger active surface per

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unit of catalyst. In some cases the use of a carrier increases the life of the catalyst by increasing its resistance to sintering at higher temperatures. The activity of a catalyst may also be improved by the presence of a so-called promoter. Promoters are substances which when mixed with the catalyst (usually in small amounts) increase its activity. The promoter may differ radically from the catalyst, in valence, ease of reduction, etc. The effects produced by a promoter probably are related to such factors as adsorption and sintering. The activity of a catalyst would be enhanced by increased adsorption and its efficiency would be materially increased if sintering effects on the surface were retarded or prevented.

Many of the vapor-phase catalytic processes used industrially, particularly those involving oxidation, are highly exothermic. Such reactions, for maximum efficiency, must be carried out within rather limited temperature ranges. The heat evolved in such reactions is liberated at the surface of the catalyst and the temperature at the surface rises considerably above that of the catalyst mass. Unless this rise can be controlled, undesirable side reactions will occur and the life of the active catalyst surface will be greatly reduced. Therefore it is essential that there should be adequate heat removal and temperature control. In practice this may be accomplished by using catalysts and catalyst supports of good heat-conducting materials and by using a liquid cooling medium circulating in direct contact with the catalyst chamber. Even measures such as these do not necessarily insure adequate conduction of heat from the center of the catalyst chamber, especially where chambers of relatively large diameter are used.

In addition to catalyst structure and heat control, a third important factor remains, namely contact time. Time of contact may be defined as the time of exposure of the reactants to the catalyst and temperature used. When the time of exposure is too prolonged, undesirable side reactions are often stimulated, resulting in a lower conversion to useful products. The success of any catalytic vapor-phase reaction must necessarily depend on a careful and detailed study of factors such as those outlined above.<sup>1</sup>

#### SILVER AS A CATALYST FOR VAPOR-PHASE OXIDATIONS

The fact that primary and secondary alcohols may be dehydrogenated to aldehydes and ketones respectively, when passed over heated metals such as copper or silver, has been known for a long time. These reactions are endothermic, requiring the addition of heat to maintain the reaction temperature. On a large scale they are not practical as the metal loses its efficiency fairly rapidly. The use of oxygen or air in these reactions to combine with the liberated hydrogen serves three purposes: (1) the removal of the hydrogen results in increased dehydrogenation of the alcohol; (2) the heat evolved in the combustion of the hydrogen is more than sufficient to maintain the temperature necessary

for dehydrogenation; and (3) the efficiency of the catalyst remains unimpaired for a longer time. Because of these obvious advantages, catalytic vapor-phase oxidation has largely replaced catalytic vapor-phase dehydrogenation.

Orloff<sup>2</sup> made the first careful study of the use of copper as a catalyst for the oxidation of alcohols. His investigations served to call to the attention of chemists the possibilities for the practical application of vapor-phase catalytic oxidations. Following the work of Orloff, the use of silver as a substitute for copper in the oxidation of alcohols was studied by LeBlanc and Plaschke.<sup>3</sup> They used silver in the form of a spiral, and also the finely divided metal precipitated upon asbestos. Their results definitely showed that silver is more effective than copper for these reactions. Fokin<sup>4</sup> studied the relative efficiencies of gold, silver, copper, platinum, cobalt, manganese, aluminum and nickel. His work demonstrated the superiority of the first three and again showed that silver is more effective than copper for the vapor-phase oxidation of alcohols.

Moureau and Mignonac,<sup>5</sup> using silver deposited on asbestos, showed that this metal is an efficient catalyst for the oxidation of the homologs of methyl alcohol. An interesting aspect of their work was the fact that the catalyst did not appear to have any appreciable decomposing influence on the products formed. For example, geraniol yielded citral without decomposition. Senderens<sup>6</sup> has also shown that silver is the most efficient of the metals for the catalytic oxidation of alcohols. Simington and Adkins<sup>7</sup> studied the catalytic oxidation of several alcohols. They found that silver gauze and a catalyst composed of 90 per cent silver and 10 per cent copper were the most efficient for the oxidation of ethyl alcohol; catalysts composed of 50 per cent silver and 50 per cent copper and 99 per cent silver and 1 per cent bismuth were the most effective for iso-propyl alcohol; and copper wire and silver gauze the most effective for *n*-butyl alcohol. Faith and Keyes,<sup>8</sup> using methyl alcohol and ethyl alcohol, studied the relative efficiencies of supported and unsupported catalysts of silver and also of copper. In the case of ethyl alcohol, an 80.6 per cent conversion to acetaldehyde was obtained using silver gauze as the catalyst, whereas with silver on asbestos the conversion dropped to 72.3 per cent. Their results indicated that the catalyst which had the greatest coefficient of heat transfer (the unsupported form) yielded the highest conversion of alcohol to aldehyde.

Lowdermilk and Day<sup>9</sup> and Day<sup>10</sup> have studied the oxidation of ethyl alcohol over copper and silver catalysts respectively. Their results definitely confirmed the superiority of silver over copper for this reaction. The reactions were carried out under similar operating conditions. Where the copper catalysts were used, the highest conversions to acetaldehyde were obtained when an excess of air was used, while with the silver catalysts the best conversions were effected when the theoretical quantity of air was employed. This would appear to indicate a greater activity on the part of the silver catalyst. The conversions of ethyl alcohol to

acetaldehyde were at least 10 per cent higher when the latter metal was used. In some of the earlier work, good results have been reported with the use of unsupported silver catalysts, such as silver gauze or pellets. From the standpoint of heat transfer, certain advantages may be claimed for the unsupported type. Day and his associates (see also Day and Eisner<sup>11</sup> and Patterson and Day,<sup>12</sup> have found in the course of their work that, in general, unsupported silver catalysts quickly deteriorate. Sintering effects are produced on the surface with the resulting decrease of active surface and operating efficiency. Two types of silver were used, silver gauze and electrolytic silver. The latter showed the results of sintering much more rapidly than the gauze, but neither maintained its efficiency after short periods of operation. To overcome these difficulties, various supporting materials for the silver were used, with the idea in mind of spreading the active points and hence decreasing their tendency to sinter. The supporting material finally adopted was specially treated 12-mesh pumice. That the objective was realized was shown by the fact that the supported catalysts retained their activity longer. The supported catalysts were prepared by the following method. The silver (2.7928 g) was deposited on 9 cc of the pumice by adding the pumice to a dilute nitric acid solution containing the equivalent amount of silver nitrate and evaporating to dryness with constant stirring. The dry material was then carefully heated, with stirring, to convert the nitrate to oxide; the latter was then heated in a stream of alcohol and air until the brown mass became gray. This catalyst, in spite of its lower coefficient of heat transfer, gave conversions of alcohol to aldehyde as high as those previously reported with the use of unsupported silver catalysts.

In the search for means of stabilizing silver surfaces for use in catalytic oxidations, the action of various promoters was also investigated. The rare-earth oxides were found to be quite effective for this purpose, when used in small amounts. In general, the rare-earth oxides are too active for the vapor-phase oxidation of organic compounds, and tend to promote complete oxidation to carbon dioxide and water. However, they possess some rather interesting properties. The oxides are easily obtained, by decomposition of the nitrates, in a highly porous form which has practically no tendency to sinter over a wide temperature range. These properties are imparted to the silver catalyst, to some extent, when a small amount of the rare-earth oxide is present with the silver. The oxide was incorporated with the silver catalyst by adding a small quantity of rare-earth nitrate to the dilute nitric acid solution of silver nitrate; the solution was then treated as previously described. The resulting catalyst surface, deposited on pumice, consisted of metallic silver interspersed with the rare-earth oxide.

During the course of the preliminary work, all the members of the cerium group were tried and appeared to be equally active. Of the

yttrium group only two, yttrium and lanthanum, were used and they appeared to be much less active as oxidation catalysts. Samarium oxide was finally adopted, mainly because of its greater porosity. The promoted catalysts had the advantage of increasing the conversion of alcohol to aldehyde and permitting efficient operation at a somewhat lower temperature. Their most important characteristic, however, was the fact that their efficiencies did not noticeably decrease over long periods of operation. The oxide appeared to serve two purposes: (1) to stimulate the activity of the catalyst; and (2) to stabilize the active silver surface by retarding or preventing sintering effects. The amount of samarium oxide used should not exceed one-half of one per cent by weight of the silver used. Above that amount there is usually an increased conversion to carbon dioxide and water.

The fact that silver has not been more widely used in commercial practice as a catalyst for vapor-phase oxidation of alcohols may be partly explained by the fact that silver surfaces have a tendency to sinter far below the melting point of the metal. This would naturally be a serious objection where long and continuous operation is necessary. This can no longer be accepted as a valid reason, for it has been shown that silver surfaces can be successfully stabilized. In view of the fact that almost all the published work has indicated the superiority of silver to copper for this type of vapor-phase oxidation, it is rather surprising that it has not been more widely applied.

There is practically no information available on the use of silver as a catalyst for vapor-phase oxidation of compounds other than alcohols. The catalytic oxidation of alcohols to aldehydes or ketones is a coupled reaction, that is, the reaction is a combination of two distinct steps. The alcohol is dehydrogenated to aldehyde or ketone, followed by the partial or complete oxidation of the hydrogen formed in the first step. The oxidation of the hydrogen furnishes the energy necessary to maintain the reaction. Silver is well suited for vapor-phase oxidations which involve dehydrogenation as the first step. For other types of oxidation, such as those involving the addition of oxygen in the first step, there is little information available. It seems to be generally believed that silver would not be a suitable catalyst for this type, although this belief does not appear to rest entirely upon experimental evidence.

Platinized silver gauze and silver platinum alloys have been used for the oxidation of ammonia.<sup>13</sup> With a catalyst composed of silver gauze coated with platinum, by means of electrolytic deposition, 99 per cent of the ammonia was said to be oxidized at 690-700 °C. This type of catalyst, however, was not thermally stable, and fusion of the gauze occurred. An alloy containing 90 per cent platinum and 10 per cent silver effected 87.9 per cent oxidation of the ammonia at 946 °C. It was noted that increasing the amount of silver in the alloy reduced its efficiency, as the resulting alloy possessed lower thermal resistance to sinter-

ing effects. It was claimed that an alloy consisting of 80 per cent platinum, 10 per cent rhodium and 10 per cent silver was thermally resistant and effected 95.7 per cent oxidation of ammonia at 935 °C.

The patent literature also contains many references to the use of silver, in mixed catalysts, for the oxidation of substances other than alcohols. For example, one patent<sup>14</sup> proposes the use of silver vanadate or arsenate as a suitable catalyst for the oxidation of side chains in aromatic hydrocarbons. The same patent claims that the vanadates, chromates, molybdates, uranates, stannates and arsenates of copper, silver, lead, thorium, cerium, nickel and cobalt greatly reduce the temperature usually required for the oxidation of anthracene when simple oxide catalysts are used. A large number of catalysts have been studied and patented for the oxidation of methane, and other gaseous paraffin hydrocarbons, to oxygenated products. It has been shown that silver on pumice becomes active as an oxidation catalyst<sup>15</sup> for methane at 320 °C, and that copper catalysts prepared in a similar way became active at 400 °C. Although some fairly good conversions of methane to formaldehyde have been reported under experimental conditions, it is doubtful if any of these procedures have been developed to the point where they could compete with the usual method of preparing formaldehyde from methyl alcohol.

These examples from the patent and published literature suggest a broader range of usefulness for silver catalysts in general. A survey of the literature indicated that the chief objection to the use of silver as a catalyst was the relative instability of silver surfaces at higher temperatures. The successful use of rare-earth oxide-promoted silver catalysts over long periods of time, however, has shown that silver surfaces can be stabilized. Further work along these lines, it is believed, will lead to a larger number of uses for silver as an oxidation catalyst.

As mentioned earlier, catalysts which have high coefficients of heat transfer have certain advantages for use in exothermic reactions, for they permit more rapid conductance of heat away from the catalyst mass. Heat transfer is so important that one must consider not only its effect within the catalyst but also its effect through the walls of the reaction chamber. Faith, Peters and Keyes<sup>16</sup> have studied the latter. Theoretically, the use of a material which is a good heat conductor should permit better heat control and hence eliminate undesirable reactions due to accumulation of excess heat. They compared the efficiency of copper tubes and "Pyrex" tubes for the oxidation of ethyl alcohol, using copper as the catalyst. With a copper block-copper tube catalyst chamber, relatively poor conversions of ethyl alcohol to acetaldehyde were obtained. This was attributed to the fact that, copper being a good heat conductor, the ends of the tube became very hot and the length of the heated zone was materially increased. To overcome this difficulty they constructed a copper-glass seal catalyst chamber. The entrance and exit tubes to the chamber were made of glass to prevent a large flow of heat along these

tubes. In this type the heat was largely confined to that part of the chamber directly in contact with the catalyst. Larger conversions were obtained with the copper-glass seal chamber, but it did not show any marked superiority over the "Pyrex" tubes. Their work, however, did point out the possibilities of this method for controlling the reaction temperature.

This survey of the literature indicated several reasons for the further investigation of silver as a catalyst for the oxidation of alcohols. It is more active than copper and operates efficiently at a lower catalyst temperature. Furthermore it appears to have a minimum tendency to promote undesirable decompositions of the reaction products. In addition to these facts, the very high thermal conductivity of silver suggested the use of silver catalysts and silver reaction chambers. It appeared quite probable that such a combination would lead to a simple method for heat control and obviate any necessity for using a liquid cooling medium to absorb the excess heat. This work was undertaken by Immediata under a grant made by the Silver Producers Research Project. The selection of the catalytic vapor-phase oxidation of ethyl alcohol for this work was prompted by the amount of information already available for comparison, the sensitivity of the reaction to temperature changes and by its possible industrial importance. The remaining portion of this chapter will be devoted to a discussion of this work.

#### USE OF SILVER CATALYSTS AND SILVER REACTION CHAMBERS IN VAPOR-PHASE OXIDATION OF ETHYL ALCOHOL

The apparatus used is shown diagrammatically in Figure 1. Dry air, measured by means of a wet-test meter, was passed through the vaporizing chamber (E) containing the ethyl alcohol (95.6 per cent by weight). The mixture of air and alcohol vapor was then passed through a "Pyrex" preheating coil, maintained at 110 °C, and thence into the catalyst chamber (G). The reaction products issuing from the chamber were passed through an absorbing train and the remaining gas was then passed through a flow meter.

Since earlier work had shown the advisability of using the theoretical oxygen-alcohol ratio, the latter was used throughout this work. This ratio was controlled by adjusting the temperature of the thermostat in which the vaporizing chamber was immersed. The theoretical ratio was obtained by working at a thermostat temperature of 54.5 °C.

The catalyst chamber, the details of which are given in Figure 2, was constructed entirely of silver. To avoid the difficulties experienced by Faith, Peters and Keyes with the copper block-copper tube chamber, provisions were made to cool the ends of the silver tube. Water-cooled jackets were used for this purpose. In this manner the heat was largely confined to that part of the chamber directly in contact with the catalyst, and consequently the reaction products were rapidly cooled on leaving the

catalyst mass. The temperature of the catalyst mass, which was measured with a thermocouple protected by a thin-walled quartz jacket, was controlled by adjusting the rates of electric heating of the catalyst bed and water-cooling of the ends of the chamber. The catalyst was electrically heated to start the reaction. As soon as the reaction started, the heat was cut off and the flow of water through the cooling jackets so regulated that the desired catalyst temperature was maintained. When the excess heat was removed too rapidly, the catalyst temperature dropped and the catalyst finally ceased functioning, due to the lack of sufficient heat to maintain the reaction. The ideal situation would be where just

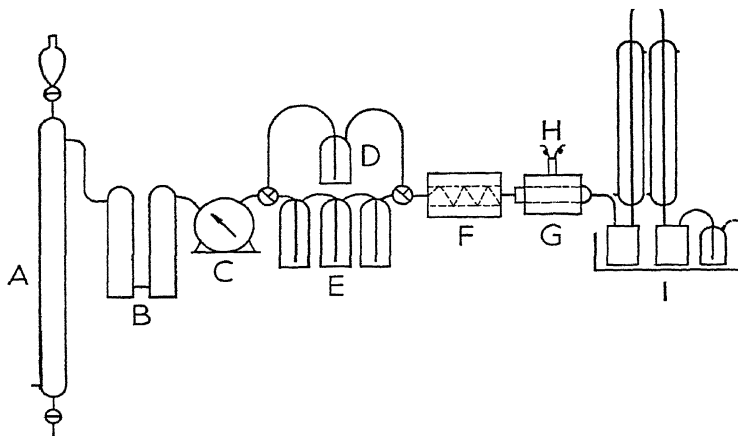


FIGURE 1. Apparatus for vapor-phase oxidation of alcohol. (A) Sulphuric acid tower. (B) Sodium hydroxide towers. (C) Wet test meter. (D) Auxiliary vaporizer. (E) Vaporizer. (F) Preheater. (G) Catalyst chamber and heater. (H) Thermocouple. (I) Absorbing train.

enough heat remains to carry the reaction. Such a delicate balance could not be obtained by the use of this method, but it is believed that most of the excess heat was removed by conductance through the silver wall and by water-cooling at the ends of the tube. This method of heat control afforded more adequate distribution and control of the heat reaction, thus preventing undue localization of heat in the active centers of the catalyst mass. The actual catalyst bed used in this work was 15 mm in length and 17 mm in diameter and was supported at each end by finely perforated porcelain plates.

In order to make a run at any given temperature, dry air was passed through the auxiliary vaporizing chamber and over the catalyst at the desired rate. The cooling rate was then adjusted to give the desired temperature. The reaction products were by-passed around the absorbing

train during this preliminary run. When the desired conditions were established, the run proper was started by passing the air through the regular vaporizing chamber and the reaction products passed through the absorbing train. Samples of gas for analysis were collected over the whole run, at such a rate that a total of approximately 500 cc was collected. Withdrawal of this sample was made after the gases had passed through the condensing system but before they entered the scrubbing system. At the end of each run, the contents of the absorbing train was made up to a definite volume and aliquots were used for analysis. The acetaldehyde was determined by Ripper's method, and the acetic acid

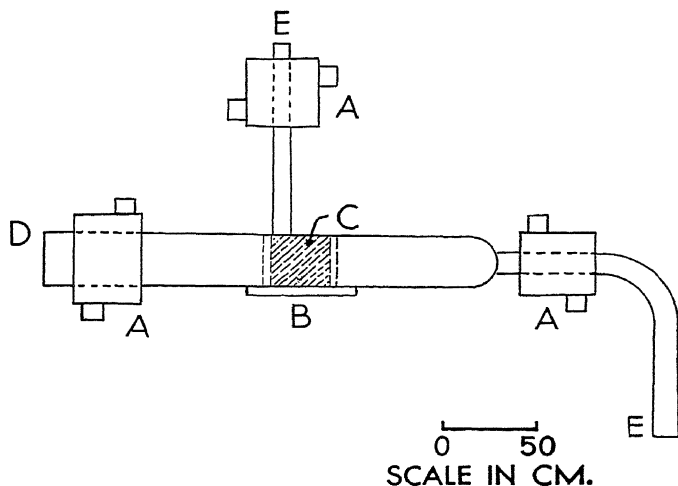


FIGURE 2. Details of the catalyst chamber. (A) Water-cooling jackets. (B) Heating zone. (C) Catalyst bed. (D) Wall thickness, 3 mm. (E) Wall thickness, 1 mm.

was determined by titrating a definite amount of standard sodium hydroxide solution, which contained a little barium chloride and a few drops of phenolphthalein solution, with the solution obtained from the absorption train.

Three types of unsupported silver catalysts were used: (1) silver precipitated from silver nitrate solutions by means of copper; (2) electrolytic silver; and (3) fine silver gauze. With these catalysts the conversions to acetaldehyde were relatively low in spite of their high thermal conductivity. The high conversions to carbon dioxide, carbon monoxide, ethylene and methane were also surprising. When higher space velocities were used, the percentage yields of useful products approached 100 per cent, but the disadvantage here was the low conversion to aldehyde. Some of the results obtained with unsupported silver are listed in Table 1.



The most undesirable features of these catalysts was their tendency to sinter at 450 °C and higher temperatures. The work with this type of catalyst showed that the best conversions were obtained at catalyst temperatures too near the sintering point of the silver surface.

Table 1.—Silver Metal.

Table I.—Silver Metal.								
Air Rate (l./min)	O <sub>2</sub> /EtOH Mole/Mole	% EtOH Converted to					% Yield CH <sub>3</sub> CHO	% Yield Useful Products
		CH <sub>3</sub> CHO	CH <sub>3</sub> COOH	CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	
Catalyst Temp. 410 °C								
0.542	0.503	44.2	1.80	7.50	0.85	2.26	0.76	80.0
0.770	0.503	49.0	2.23	6.92	1.10	2.30	0.92	81.7
1.14	0.528	45.0	2.40	3.85	1.00	1.20	0.87	87.4
1.31	0.560	38.5	2.20	1.00	0.56	0.50	0.24	94.5
Catalyst Temp. 430 °C								
0.734	0.509	47.4	2.68	10.5	2.82	2.68	1.98	73.5
1.48	0.630	63.8	3.68	10.9	2.62	1.52	2.41	79.6
1.92	0.504	65.8	3.92	1.71	0.99	0.76	1.46	94.9
2.10	0.495	56.3	2.40	1.25	1.04	0.00	0.42	95.7

The performance was greatly improved when the silver was used on pumice as a support (Table 2). Conversions to aldehyde of 80 per cent and total conversions to aldehyde and acetic acid of 86 per cent were obtained in the temperature range of 400-500 °C. The supported catalyst appeared to be rather resistant to sintering at 470 °C. At 500 °C or above, sintering effects were noted and the catalyst became less active. The lower limit for the supported as well as the unsupported catalysts was about 400 °C. Below that temperature the catalytic activity was greatly diminished. The experimental data showed clearly that the supported catalyst was somewhat more resistant to sintering effects and consequently can be used at higher temperatures. Since the conversion to gaseous products was virtually the same as with the unsupported catalyst, these data are not included in Table 2.

Table 2.—Silver on Pumice.

Air Rate (l/min)	O <sub>2</sub> /EtOH Mole/Mole	% Conversion CH <sub>3</sub> CHO	Air Rate (l/min)	O <sub>2</sub> /EtOH Mole/Mole	% Conversion CH <sub>3</sub> CHO
Catalyst Temp. 410 °C			Catalyst Temp. 500 °C		
0.406	0.945	81.0	0.820	0.552	56.7
0.558	0.990	76.1	1.26	0.583	66.8
0.680	0.874	73.5	1.50	0.582	80.2
0.972	0.924	68.8	2.73	0.590	73.0
			3.51	0.592	59.2
Catalyst Temp. 470 °C					
	Air Rate (l/min)	O <sub>2</sub> /EtOH Mole/Mole		% Conversion CH <sub>3</sub> CHO	
	Catalyst Temp. 470 °C				
	0.450	0.548		70.7	
	0.700	0.581		78.0	
	0.810	0.586		76.4	
	1.12	0.584		66.5	

The activity and performance of the samarium oxide-promoted catalysts were uniform to a marked degree. With these catalysts, operation

for long periods of time at 490-500 °C was possible without the appearance of sintering. The promoted catalysts were prepared by adding 12-mesh pumice to a solution containing silver nitrate and samarium nitrate, and evaporating this mixture to dryness, with constant stirring. The amounts of nitrates taken were equivalent to 0.33 g of a mixture of silver oxide and samarium oxide for each cc of pumice. Samarium oxide was present to the extent of one-eighth or one-quarter of one per cent. The dry material was then carefully heated to decompose the nitrates to oxides and the latter were then heated in a stream of air and alcohol vapor (at 400 °C) to reduce the silver oxide to metal. The results from the use of this type of catalyst are listed in Tables 3 and 4. A study of these tables

Table 3.—Silver + 0.125%  $\text{Sm}_2\text{O}_3$  Catalyst.

Air Rate (l/min)	O <sub>2</sub> /EtOH Mole/Mole	Table 3.—Silver + 0.125% Sn <sub>2</sub> O <sub>3</sub> Catalyst.						% Yield CH <sub>3</sub> CHO	% Yield Useful Products
		CH <sub>3</sub> CHO	CH <sub>3</sub> COOH	% EtOH CO <sub>2</sub>	Converted to CO	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>		
Catalyst Temp. 340 °C									
1.32	0.500	63.8	4.48	1.48	0.28	1.00	1.38	88.0	94.3
1.52	0.502	73.6	4.72	0.82	0.18	2.55	1.10	88.7	94.5
1.70	0.504	71.3	3.90	0.17	0.75	0.26	1.00	92.2	97.3
Catalyst Temp. 430 °C									
1.40	0.501	74.0	4.62	8.00	0.18	7.58	4.20	75.1	79.8
1.64	0.509	81.0	4.80	2.82	0.38	0.85	0.00	90.0	95.4
2.24	0.508	70.0	4.23	4.15	0.38	0.77	1.47	86.4	91.6
Catalyst Temp. 460 °C									
1.18	0.500	77.6	3.81	7.10	1.40	0.40	3.80	82.7	86.6
1.48	0.501	76.0	4.77	5.10	0.81	0.21	0.00	87.6	93.0
1.87	0.504	75.8	3.82	3.47	1.95	0.00	1.30	87.7	92.2
1.95	0.505	80.0	4.84	5.20	0.86	0.86	1.28	86.1	91.2
2.21	0.507	75.0	4.77	8.00	1.75	0.34	1.42	82.3	87.5
Catalyst Temp. 490 °C									
2.33	0.508	60.3	5.25	8.12	0.00	0.70	3.74	77.4	84.0
2.56	0.508	65.8	5.13	8.45	2.20	0.10	3.52	77.4	83.2
3.10	0.508	67.8	4.67	7.10	1.55	0.93	3.00	79.7	85.2

discloses some interesting facts. The promoted catalysts were active at a much lower temperature, and fairly good conversions to acetaldehyde were effected at temperatures as low as 340 °C, the percentage yields of useful products being very high at this temperature. At higher catalyst temperatures, higher conversions to aldehyde were obtained. Under operating conditions where conversions to aldehyde were high (80-84 per cent) the total conversions to acetaldehyde and acetic acid approached 90 per cent. At the same time it will be noted that conversions to carbon dioxide remained relatively low. The temperature limits for satisfactory operation with these catalysts were quite wide, offering a large margin for fluctuation without materially affecting the results. The use of the promoted silver catalysts and a silver reaction chamber is an efficient combination from the standpoint of the conversion of ethyl alcohol to useful products. This type of catalyst not only functions at lower tempera-

Table 4.—Silver + 0.25% Sm<sub>2</sub>O<sub>3</sub> Catalyst.

Table 4.—Silver + 0.25% Sm <sub>2</sub> O <sub>3</sub> Catalyst.									
Air Rate (l/min)	O <sub>2</sub> /EtOH Mole/Mole			% EtOH Converted to				% Yield CH <sub>3</sub> CHO	% Yield Useful Products
		CH <sub>3</sub> CHO	CH <sub>3</sub> COOH	CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>		
Catalyst Temp. 340 °C									
0.875	0.540	58.3	2.80	3.09	0.24	1.00	0.42	88.5	92.8
1.02	0.542	69.4	3.44	1.83	0.10	0.36	1.04	91.3	95.7
1.37	0.501	77.6	3.59	1.53	0.14	0.92	1.07	91.6	95.8
1.57	0.501	47.2	1.66	0.86	0.09	0.87	1.00	91.4	95.0
Catalyst Temp. 380 °C									
0.945	0.499	56.8	2.45	5.00	1.05	0.04	0.25	86.8	90.4
1.37	0.501	77.0	3.70	4.15	0.84	0.76	0.42	89.0	92.8
1.68	0.504	74.3	3.11	3.91	0.66	1.37	1.00	88.3	91.8
2.00	0.504	65.0	3.82	3.24	0.36	0.64	0.18	88.7	92.8
Catalyst Temp. 430 °C									
1.84	0.505	71.5	4.72	7.05	0.42	0.00	0.08	85.3	90.9
2.07	0.507	73.8	5.63	5.57	0.46	0.10	0.22	86.0	92.5
2.27	0.508	84.0	5.02	7.20	0.24	0.00	0.16	86.1	91.2
2.67	0.510	65.0	3.85	5.15	0.22	0.09	0.07	86.2	92.8
Catalyst Temp. 460 °C									
2.33	0.508	70.3	3.20	7.40	1.02	0.32	0.56	84.9	88.7
2.51	0.508	77.5	4.06	7.00	1.31	0.70	0.71	84.9	89.4
2.90	0.509	72.0	3.36	4.30	1.20	0.40	0.60	87.9	92.1
3.01	0.501	60.3	2.47	4.02	0.91	0.36	0.45	88.0	91.7
Catalyst Temp. 490 °C									
1.84	0.508	60.0	5.24	10.2	1.20	0.82	2.10	75.5	82.0
2.73	0.506	64.5	5.53	10.5	1.37	0.76	2.17	76.1	82.5
2.67	0.508	61.0	4.70	10.5	1.22	0.61	2.11	76.2	82.0
3.01	0.510	50.0	3.00	10.1	1.08	0.60	1.90	75.0	79.5

tures but it permits working under conditions where high conversions and high percentage yields are obtained. Thus the amount of alcohol to be recovered and reprocessed would be small. The samarium oxide-promoted silver catalysts have given the highest conversions and the most consistent results thus far reported in the literature. A catalyst promoted with one-half of one per cent samarium oxide gave lower conversions to useful products. For the oxidation of alcohols, the use of more than one-quarter of one per cent of samarium oxide is not desirable.

The production of acetic acid by the vapor-phase oxidation of acetaldehyde or ethyl alcohol would be of some interest. Many attempts<sup>17</sup> to accomplish this have been reported, but most of them have failed. Some of these are described in the patent literature, but there appears to be no way of determining whether or not they have been successful in actual practice. Immediata carried out some preliminary experiments on the conversion of ethyl alcohol and acetaldehyde to acetic acid. As this work was discontinued at the termination of the fellowship, a complete study was not made. Some of the results from his preliminary work were rather interesting and will be reported here. These experiments were carried out with the silver catalysts and silver reaction chamber previously described. The attempts to convert the alcohol to acid in one

operation were unsuccessful. It was noted that the yields of acetic acid were no higher than the yields obtained in the alcohol to aldehyde reaction. The gas analyses showed that large losses (up to 50 per cent) occurred through pyrolysis of the aldehyde to methane and carbon monoxide. In other runs acetaldehyde was used as the starting material but with no better results. Here, however, it was noted that an exothermic reaction took place in the preheater whenever it was heated to 150 °C or above, and a high conversion to methane resulted. That the rate of the

Table 5.—Oxidation of  $\text{CH}_3\text{CHO}$  to  $\text{CH}_3\text{COOH}$ 

Air Rate (l/min)	$\text{O}_2/\text{CH}_3\text{CHO}$ Mole/Mole	Temp. (°C)	% Converted $\text{CH}_3\text{COOH}$	% Recovered $\text{CH}_3\text{CHO}$	% Yield $\text{CH}_3\text{COOH}$
1.80	0.600	250	Traces	58.6	—
3.00	0.506	280	2.88	52.0	6.00
2.20	0.468	300	3.00	50.0	6.00
1.76	0.500	310	3.08	43.2	5.42
2.88	0.626	340	2.72	52.2	5.68
3.12	0.630	400	4.68	46.6	8.77

thermal decomposition of gaseous acetaldehyde is considerably accelerated by even traces of oxygen has been reported by Letort.<sup>18</sup> This low-temperature pyrolysis is most significant, since any directive catalyst for the desired oxidation would have to function at a temperature lower than 150 °C, at least at normal pressure. Some of the preliminary results from the attempts to oxidize acetaldehyde are shown in Table 5.



## Chapter 15

### Corrosion Resistance of Silver and Silver Alloys

BY ALLISON BUTTS \* AND J. M. THOMAS †

The ability to resist corrosion is one of the properties of silver most favorable for increased use of the metal in industry. The aim of this chapter is to summarize all the important data that have been published concerning the resistance of silver to corrosion by all the important industrial chemicals, in order to make the information readily available for consideration in any projected use of silver as a structural material or a coating in the manufacture, storage, shipment, or use of any of the chemicals in question. Included in the data presented will be the results, not previously published, of a series of laboratory corrosion tests made by the writers in the metallurgical department at Lehigh University.

A brief discussion of the theoretical aspects of the corrosion resistance of silver will first be profitable. There must also be pointed out limitations in the uncritical acceptance of corrosion data, the usefulness of which depends on the conditions of the tests under which they were obtained and the variation of those conditions from those of industrial application.

The relative corrodibility of metals in general is determined primarily by two things: first, the position of the metal in the electropotential series; and secondly, the formation or lack of formation of a protective film on the surface of the metal. With any particular metallic object, the first of the above factors must be thought of as including not only the standard potential of the metallic element, but also the purity of the metal as it exists in the object in question and especially its homogeneity, both chemical and physical, lack of which will establish local galvanic couples on its surface and either initiate or accelerate corrosion. In the second factor the characteristics of the film are of the greatest importance—whether it is porous or non-porous, continuous or broken, adherent or non-adherent, slow-forming or quickly “self-healing,” soluble or insoluble in a liquid with which it may be in contact.

In addition to the two factors just named, which apply to the metal itself, the surroundings are a determining factor. The potential difference causing corrosion depends as much on the liquid or gas in contact with the metal as it does on the metal itself. This matter, however, need

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not be discussed here in a special consideration of silver, except in so far as the surroundings may include another metal in contact with silver.

The excellent corrosion resistance of silver is founded chiefly on the first of the above two factors, that is, on its high degree of nobility. Film formation on silver is rarely of importance in inhibiting corrosion, though in a few cases it is a factor, as for example the formation of a silver chloride coating in hydrochloric acid. Silver thus falls in the class with gold and platinum as regards corrosion resistance, and differs essentially in this respect from such metals as aluminum, chromium, and stainless steel, the corrosion resistance of which is due to a surface film normally invisible. Usually, therefore, since silver does not depend primarily on a surface condition for its corrosion resistance, the user need not be concerned with conditions which might remove or break a protective film, such as chemical solution of it, or wear or abrasion of it by movement of a liquid in contact. There are exceptions, however, in the case of some chemicals.

Atmospheric corrosion is manifested in oxidation by air in the presence of moisture, often supplemented by carbon dioxide and occasionally by some other gas present in the atmosphere. Since silver does not oxidize under atmospheric conditions, it is entirely immune from atmospheric corrosion (unless one includes under "atmospheric corrosion" possible attack by chemical fumes present somewhere in unusual concentration). Excluded also must be the well-known tarnishing of silver by a sulfur compound (usually hydrogen sulfide) in the atmosphere; this will be discussed further on.

The standard potential of silver is 0.80 volt, in normal ionic solution at 25 °C, being much higher than that of copper (0.34 volt), practically the same as that of mercury (0.80 volt), and exceeded only by those of platinum (0.86 volt) and gold (1.36 volt). These figures indicate that in the establishment of a galvanic couple between silver and any other common metal except mercury, platinum, or gold, assuming perfectly clean metallic surfaces and the absence of some unusual chemical factor, silver will be cathodic and therefore not corroded. Even in a couple with a metal protected by a film, such as aluminum, chromium, or stainless steel, in which case silver will be potentially anodic, the potential difference will be small, the film will tend to reduce flow of current, and the resulting corrosion of silver, if it occurs at all, will be correspondingly low.

Although the chemical nobility of silver is thus highly conducive to corrosion resistance, it is at the same time unfavorable for the formation of a protective film. Only in liquids or vapors which will react with silver to form an insoluble compound, such as silver chloride, may the formation of a film be of value.

The nobility of silver is also unfavorable from another standpoint, namely in the case of a silver coating that is not entirely continuous

and free from pinholes. Silver plating done by ordinary methods is usually of this character, and while the defect may be of no consequence for atmospheric exposure indoors or other conditions of only mild corrosive influence, it must nevertheless be borne in mind that such a plating produces a galvanic cell in which the basis metal becomes anode. As a result, in so far as air and moisture may penetrate the coating and reach the basis metal, a condition accelerating to corrosion of the base (though protective to the silver) is caused.

The utmost caution must also be exercised in the use of silver as a structural part in contact with less noble metals, lest it cause them to become anodic in a couple strongly conducive to corrosion. The high electrical conductivity of silver and its freedom from film may be contributing factors in an improper design of this kind.

Silver is strongly resistant to atmospheric and ordinary oxidation, and is exceptionally resistant to corrosion by weak acids and most organic compounds, including those commonly met in food products. There are, however, numerous exceptions to its corrosion-resisting qualities. It is dissolved readily by nitric acid and by hot concentrated sulfuric acid. It is attacked by strong halogen acids, including concentrated hydrochloric; also by cyanide solutions, by sulfur and many of its compounds, and by mercury and its compounds. This statement is made here to emphasize the danger of too much general inference as to the corrosion resistance of silver; the individual effects of the various substances will be noted in the pages which follow.

### Corrosion Testing \*

Methods of corrosion testing in common use include prolonged exposure to current atmospheric conditions; salt-spray tests; electrolytic tests, usually with the specimen as anode and with or without applied potential; time-potential measurements; simple immersion, either total or partial, in the latter case with particular attention to corrosion at the metal-liquid-air or metal-liquid-vapor junction, under still conditions; the same under conditions of flow or motion of the corroding liquid; and refluxing of boiling solutions. The work of experienced investigators has led them to the conclusion that the results of corrosion tests are of relatively little value unless all the conditions of the tests are suitably controlled and reported. Even at best, the results under test conditions may be at wide variance with results in actual plant installations, particularly when the test has been for only a short period relative to prolonged industrial use. Initial attack by a chemical may be very different from, often much greater than, the attack which ensues on further con-

\* For more detailed discussion, see R. M. Burns and A. E. Schuh, "Protective Coatings for Metals," pp. 234-274, Reinhold Publishing Corporation, New York, 1939. "Symposium on Corrosion Testing Procedures," Am. Soc. Testing Materials, 1937.

H. E. Searle and F. L. LaQue, *Proc. Am. Soc. Testing Materials*, 35, pt. 2, 249 (1935).



tact; this is especially true when a film is formed. The best procedure in testing corrosion by chemicals is to divide the exposure into suitable initial and subsequent test periods. The general experience has been that accelerated corrosion tests do not reliably represent the results in long-time service.

Not only is there variation between laboratory test and service results, but there is also much discrepancy between test data published by different investigators on similar corrosion problems. Among the factors which cause variations and discrepancies are differences in purity of the metal samples; difference in physical condition of the metal samples (whether rolled or cast, etc.); differences in homogeneity; differences in surface conditions and methods of preparation of metal samples; differences in purity of chemicals; polarization and depolarization of electrochemical reactions; differences in the relative size of anodic and cathodic areas; differences in concentration and in temperature of chemical corroders; solubility of corrosion products and the effect of this, together with concentration and temperature, on equilibrium in a chemical corroding reaction; flow or motion of the corrodent and its effect both on equilibrium and on abrasion of a film; differences in the time of test periods; aeration and its pronounced effect on film formation; treatment of samples before weighing; effects of surroundings (including stray currents, contact with other metals, dirt, and fumes in industrial plants); and the combined or cumulative effects of two or more factors as distinguished from their individual effects.

With all these possible variations, it is not surprising that the results of tests must be accepted with reserve in all cases, and especially so when important factors are uncontrolled or unreported. Nevertheless, when even a simple test properly conducted shows a metal to be subject to serious attack, it may be concluded that this metal will be at least unreliable and probably seriously deficient in service. A favorable test result, on the other hand, while not conclusive as to adoption for use, indicates that further investigation and perhaps pilot-scale testing are in order. Comparative tests of different metals under identical conditions may be especially valuable.

It should be remembered that silver, like other metals, may corrode even when pure, clean, homogeneous, and isolated from other metals due to differences in concentration of a solution at different points of contact with the metal. It has been stated<sup>156</sup> that a potential over 0.5 volt has been measured between silver electrodes in silver solutions of readily obtainable concentration differences. While pure concentration cell potentials are normally very much smaller than this, they are important causes of corrosion.

The reports given in this chapter are made with the foregoing facts in mind. It is believed that they will be useful as initial guides, but they should not of themselves be made the bases of final recommendations.

In the tests made at Lehigh University, comparison of silver with other metals in attack by certain important industrial chemicals was the usual object sought. Especially in the chemical industry, it appeared that the greatest need for a corrosion-resistant material was evidenced in handling corrosive materials at temperatures well above room temperature. Metals are needed which will resist attack even in the vapor over a boiling solution. In order to test many materials in a limited time, a simple type of test was necessary, but at the same time it was desired to select a method which would simulate conditions likely to be encountered in chemical manufacturing operations and yet would be affected as little as possible by variations in conditions and thus necessitate a minimum of regulating control. The method adopted was one of refluxing in closed glass vessels, with some samples totally immersed in the boiling liquid, some suspended in the vapors above the liquid, and some at the liquid-vapor junction. Due attention was given also to results after a relatively short initial period and subsequent corrosion after ensuing longer periods. Details of the test conditions are given in the following paragraphs to minimize the necessity of repetition under the individual reports which follow along with the results obtained by other investigators.

The corrosive substances used in making the tests were either of a chemically pure reagent grade or were chemicals supplied by coöperating companies. The metal test specimens were secured from leading commercial manufacturers of those metals. Only metals which are commercially available were tested. The compositions of the various metals are given below.

*Silver:* High-purity silver foil (999.9 fine), 0.002 in. thickness; and 999.7 fine, 50-ml crucibles.

*Nickel:* Standard cold-rolled A nickel sheet, 0.025 in. thickness, complete-temper soft; also nickel crucibles, 99.86 per cent Ni.

*Aluminum:* 3S-1/4H flat sheet containing 1-1.5 per cent Mn, .062 in. thickness.

*Copper:* Electrolytic sheet, half hard, 0.016 in. thickness.

*18-8 Stainless Steel:* 0.10 per cent C, 0.25 per cent each Mn and Si, 0.01 in. thickness.

*Iron:* Commercially available 50-ml crucibles.

*Hastelloy B:* Nickel-molybdenum-iron alloy. Sheet of 0.06 in. thickness.

*Silver Alloys:* Silver-rich alloys of arsenic, antimony, aluminum, silicon, and manganese.

The metal samples were degreased with benzene, scrubbed with powdered pumice, washed first with distilled water and then with alcohol, and dried in a warm air blast.

A somewhat roughened surface resulted when the metal was scrubbed with wet pumice. The writers believe that the increased surface area

thus exposed to corrosion will more nearly simulate actual conditions than will a highly buffed surface. Commercial manufacturers frequently present corrosion test results that are questionable because they are based on the attack on buffed specimens. It has been found also that buffed surfaces are contaminated by incorporation of the polishing agent, and that this will affect corrosion resistance sometimes beneficially and sometimes otherwise.

The usual testing apparatus consisted of a one-liter, three-neck, round-bottomed flask in the outer necks of which were connected two vertically placed Liebig condensers. The center opening of the flask was stoppered and contained thermometers for the measurement of the liquid or vapor temperatures.

A sample of 500 ml of the corrosive substance was placed in the flask. Samples designated as "A" samples, 10 by 1 cm, were suspended from glass rods inside the inner tube of the water-cooled condenser, entirely in the vapors. "B" samples were suspended on a glass hook at the junction of the liquid and vapor phases. These samples were approximately 10 by 1.5 cm, of which about one-third was in contact with the vapor phase. "C" samples were 10 by 2.5 cm and were completely immersed in the liquid.

The corrosive material was as a rule held at a slow boil, the resulting vapors condensing after coming into contact with the "A" samples.

Under the standard procedure, free access of air was allowed to the condenser tubes when the vapor condensed.

After having been exposed to a corroding medium under specified conditions, the samples were washed with water, and then rubbed lightly with Bon Ami and cotton to remove any loosely adherent corrosion product. They were then washed again with distilled water and with alcohol, dried in a warm air blast, and then weighed.

Both the contamination of the refluxed material and also the corrosion or disintegration of the metal are important industrially. The changing physical and chemical properties, especially color changes and boiling point variations, of the corrodent were observed. The corrosion of the metal was indicated in the weight loss of a sample; the weight loss is represented both in per cent and in mg/sq dm/day (abbreviation, mdd.). Corrosion rates in inches of penetration per year may be calculated as follows:

$$\text{Mg/dm}^2/\text{day} \times \frac{.001437}{\text{density}} = \text{inches/year}$$

Tests were run for varying lengths of time, depending to a great extent upon the amount of corrosion taking place. However, in all cases a record of the original weight and the weight after a period of 24 hours of testing was made. In describing the results of a 24-96 hour test, for example, the "original" weight is the weight recorded after 24 hours of

initial test. In many tests, corrosion is much more rapid during the first period than subsequently, and continued testing does not show progressive weight losses.

#### RESISTANCE OF SILVER TO CORROSION BY VARIOUS SUBSTANCES

The corrosion resistance of silver to a large number of substances, chiefly industrial chemicals, will now be outlined briefly. Significant data will be quoted and references from the literature cited. This information will be arranged under the heads of the various materials in alphabetical order.

The following preliminary tabulation lists the substances considered, together with literature references pertaining to the corrosion resistance of silver by each of them. Only the more important of these references are quoted in the discussion which follows after the tabulation.

An asterisk (\*) preceding an item in this listing indicates that the corrosion resistance of silver to this substance is satisfactory under certain conditions, though not necessarily so under other conditions.

Corroding Agent	Reference Source (See Bibliography)
* Acetate rayon	2, 7, 26, 28, 56, 72
* Acetic acid	2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 26, 27, 28, 56, 72, 73, 115, 118
* Acetic anhydride	14
* Acetone	2, 9
* Acetyl salicyelic acid	15
Acetylene	6, 10, 74
Alkali cyanides	2, 10, 16
Alkali sulfides	2, 16
* Alum	2
* Aluminum sulfate	2, 3
* Ammonia	2, 6, 10, 14, 17, 26, 120
* Ammonium carbonate	6
* Ammonium chloride	2, 3, 6, 10, 21, 75
* Ammonium hydroxide	6, 10, 14, 16, 17, 21, 27, 33
Ammonium-hydroxide-chloride mixture	14
Ammonium polysulfide	6
* Ammonium sulfate (sat.) plus 5% sulfuric acid	2
* Aniline dyes	14
* Aqua regia	6, 17, 18, 37, 141
* Artificial silk	See Acetate rayon
* Atmosphere	6, 10, 14, 53, 76, 106
Barium peroxide	18
Benzaldehyde	6, 7, 10, 77
* Benzoic acid	5, 8, 9, 19, 26, 28, 56, 72
* Beverages	5, 7, 14, 15, 19, 148
* Bismuth oxide	18
Bleaching powder	2
Borax, fused	7, 18
* Boric acid	2
* Brewery fluids	6, 15, 19, 123, 127, 148
Bromic acid	10, 18
Bromine	2, 6, 10
Bromine-vapor mixture	14

Corroding Agent	Reference Source (See Bibliography)
* Calcium carbonate	18
* Carboic acid	See Phenol
* Carbon dioxide	7
* Carbon disulfide	6, 7, 10, 18, 21, 39, 75
* Carbon monoxide	7, 18, 21, 22
* Carbon tetrachloride	2, 128
* Carbonates	6
* Carbonic acid	7, 18
* Cesium hydroxide	18, 20
* Chloracetic acid	23
<i>p</i> -Chlorbenzaldehyde	6, 10, 75
Chlorates (alkali metals)	6
Chloric acid	6, 10, 18, 24, 25
* Chlorine	6, 7, 10, 16, 18, 26, 28, 56, 72, 77, 78, 130
Chlorine vapor-mixture	14, 108
Chromic acid	6, 25, 142, 146
* Cider	15, 28
* Citric acid	7, 16, 125
* Coal-tar products	14
* Copper oxide	10
* Cupric chloride	2, 6, 7, 10, 18
* Cupric nitrate	7, 10, 18, 27, 28
* Cupric sulfate	10
* Cupric sulfate-sulfuric acid solution	
Cuprous chloride	7, 27
Cuprous nitrate	7, 28
Cuprous sulfate	7
* Cyanogen	18, 153
* Dairy products	15
* Dyestuffs	2, 14, 28, 56, 72, 79, 139
* Essential oils	14, 15, 19, 79
* Ether (ethyl)	2
* Ethyl chloride	2
* Fatty acids	2, 6, 7, 10, 18, 28, 29, 113
Ferric alum	27, 146
Ferric ammonium alum	27, 146
* Ferric oxide	18, 146
Ferric sulfate	6, 7, 18, 146
Ferrous ammonium sulfate	6, 27
Ferrous sulfate	6, 7
* Fluorides	15
* Fluorine	6, 10, 18, 30, 31, 80
* Foodstuffs	6, 7, 10, 14, 19, 32, 84, 109, 121, 129
* Formaldehyde	2, 15
* Formic acid	2, 16, 79
* Fruit juices and extracts	7, 14, 19
* Gelatin	7, 10, 32, 119
Glass (molten)	18
* Glue	7
* Glycerin	14
* Halogen gases	6, 16, 18, 114, 117, 140; see also specific halogens.
Hydriodic acid	6, 10, 16, 18
Hydrobromic acid	6, 7, 16, 18
* Hydrochloric acid, dilute	2, 6, 7, 10, 15, 18, 21, 26, 27, 28, 33, 34, 56, 72, 78, 79, 81, 104, 105
* Hydrofluoric acid (aqueous)	6, 7, 14, 16, 18, 21
* Hydrogen	6, 18
* Hydrogen chloride	6, 18, 21; see also Hydrochloric acid.
Hydrogen peroxide	6, 12, 18
Hydrogen selenide	14, 18
Hydrogen sulfide	18, 77, 82, 83, 135, 140, 143

Corroding Agent	Reference Source (See Bibliography)
Hypochlorous acid	18, 150
* Ink	14, 28, 56, 72
Iodic acid	15, 18, 25
* Iodine solution	2, 10, 35
Iodine in potassium iodide	2
* Iron oxide	10, 18
Iron sulfate	10
* Jellies	14, 15
* Lactic acid	2, 14, 107
* Lead oxide	7, 10, 18
Lead peroxide	18
* Magnesium chloride	2
* Magnesium sulfate	2
* Malic acid	7
Mercuric chloride	6, 10, 18, 27
Mercurous chloride	6, 10, 18
Mercuric iodide	6, 18
Mercury	6, 10
* Mine waters	15
Nitrate fusions	6
Nitric acid	6, 10, 18, 27, 36, 85, 116, 124, 131, 147, 149, 151, 155
* Nitric oxide	7, 10, 18, 21, 86
Nitric-sulfuric acid (mixed acids)	2, 10
* Nitrogen	6, 10, 18, 39
Nitrogen tetroxide	7, 87
* Nitrosyl chloride	6, 7, 10, 37
* Oleic acid	2; see also Fatty acids.
* Organic acids	6, 9, 26, 28, 56, 72, 84
* Oxalic acid	14, 16
* Oxygen	6, 10, 14, 16, 18, 38, 39, 53, 88, 138
Ozone	6, 14, 18, 40, 89, 136
* Palmitic acid	6; see also Fatty acids.
* Pectin	7
Persulfate solutions	41, 90
* Pharmaceuticals	7, 15
* Phenol	1, 6, 8, 14, 15, 19, 28, 42, 43, 44, 56, 79, 144, 145
* Phosphates	15
* Phosphoric acid	2, 6, 16, 110, 126
* Photographic emulsions	7, 28, 56, 72
* Phthalic acid	6, 8, 9, 19, 26, 28, 56, 72
Potassium bromide	2, 10, 18
Potassium chloride	2, 10, 18
Potassium cyanide	6, 10, 18, 91, 97
* Potassium dichromate	6
Potassium ferrocyanide	10, 18
* Potassium hydroxide	10, 16, 18, 20, 45, 50
Potassium iodide	2, 10, 18
Potassium nitrate	2, 18
Potassium permanganate	6, 18
Potassium peroxide	6, 10, 18, 92, 152
Potassium persulfate	6, 10
Potassium sulfide	10, 18
* Propionic acid	15
Pyrosulfuric acid	14, 87
* Rayon	See Acetate rayon
* Rubidium hydroxide	6, 17, 18, 20
* Salicylic acid	5
* Sea water	6, 47, 102, 103, 112, 154
Selenic acid	6, 10, 18
* Sodium bicarbonate	7, 10, 18, 22
* Sodium borate	6, 7, 10

Corroding Agent	Reference Source (See Bibliography)
Sodium bromide	7
* Sodium carbonate	6
* Sodium chloride	2, 10, 16, 48, 49, 93
Sodium chloride, fused	7, 10
Sodium cyanide	7, 10, 16
Sodium ferrocyanide	7
* Sodium hydroxide	2, 6, 10, 14, 15, 16, 18, 20, 45, 50, 51, 52, 81, 94, 95, 107
* Sodium iodide, fused	7
* Sodium nitrate	6
Sodium peroxide	6, 18, 49, 96, 98
Sodium persulfate	10, 41
* Sodium phosphate	7, 10, 14
Sodium polysulfide	6
* Sodium sulfate	2
Sodium sulfide	7
Sodium thiosulfate	2, 6, 7, 15
* Steam	See Water vapor
* Stearic acid	6, 7, 18, 29; see Fatty acids
Sulfur	2, 6, 10, 18, 53, 99, 134
* Sulfur dioxide	6, 18, 100
* Sulfur monochloride	54
Sulfur trioxide	6, 46
* Sulfuric acid	1, 2, 6, 10, 16, 18, 21, 25, 27, 55, 56, 100, 111, 122
* Sulfurous acid	100
* Sulfuryl chloride	6, 57
* Tanning solutions	14, 58
* Tartaric acid	7
* Tetraethyl lead	15
<i>p</i> -Toluyaldehyde	6, 10, 77
* Trisodium phosphate	14
* Urea	6, 15, 59
* Vinegar	See Acetic acid
Viscose	2
* Water	6, 14, 18, 21, 39, 60, 61, 101, 132, 133, 137
* Water vapor	6, 10
* Wines	62
* Zinc chloride	2
* Zinc oxide	18

**Acetate Rayon.**—Silver condensers have been successfully used in many plants for the recovery of various corrosive solvents used in the manufacture of acetate rayon.<sup>1</sup> Silver and silver-alloy valves, cocks, and taps have found considerable use in the dyestuff plant in this manufacture.<sup>2</sup>

**Acetic Acid.**—Few metals are resistant to the attack of acetic acid. Hatfield<sup>3</sup> observed the attack of 33-per cent acetic acid on twenty-one commercial metals and alloys when the metal samples were completely immersed. All the samples tested, which included various steels, Monel, aluminum, the brasses, and the bronzes, were attacked by the acid. Hatfield, Monypenny, Kayser, and Arnott<sup>4</sup> all state that stainless steel is unsatisfactory in its resistance to acetic acid attack. Nickel-chromium alloys have a much better resistance, although they, too, are attacked in the boiling solution.

Aluminum, nickel, copper, and silver have been used in the handling of acetic acid. The corrosive action of acetic acid is of utmost impor-

tance upon condensation and subsequent handling of the concentrated acid. It has been suggested<sup>2</sup> that the high degree of corrosion may be due to finely divided acid and oxygen; this has been a source of a great amount of trouble to the manufacturers who usually use copper.

Table 1.—Weight Losses of Metal Samples in Glacial Acetic Acid (99.5%) in mg/sq dm/day (mdd) (+ = gain)

	Silver		Nickel		Aluminum	
	%	mdd	%	mdd	%	mdd
0-24 hour test						
A (in vapor)	0.20	5.0	0.30	75.0	0.05	10.0
B (at junction)	.20	6.0	.65	190.0	.36	75.0
C (in liquid)	.10	2.5	.30	75.0	+ .20	+ 38.0
Color of solution	unchanged		slight green		yellow	
Precipitate	none		none		small amount	
24-48 hour test						
A (in vapor)	0.10	2.0	0.20	55.0	0.00	0.0
B (at junction)	.40	10.0	2.00	600.0	3.00	600.0
C (in liquid)	.70	20.0	.45	130.0	+ .20	+ 40.0
Color of solution	unchanged		green		yellow	
Precipitate	none		green and black		voluminous white	
48-120 hour test						
A (in vapor)	0.30	2.5	2.80	270.0		
B (at junction)	.30	2.4	3.50	300.0		
C (in liquid)	.00	0.0	1.00	100.0		
Color of solution	slight amber		green			
Precipitate	none		green			
120-144 hour test						
A (in vapor)	0.20	6.0	0.40	100.0		
B (at junction)	.26	6.0	.90	230.0		
C (in liquid)	—	—	.50	150.0		
Color of solution	amber		green			
Precipitate	none		green			
24-210 hour test						
A (in vapor)	0.90	3.0	3.90	140.0		
B (at junction)	1.54	4.8	8.30	300.0		
C (in liquid)	.90	3.0	3.60	130.0		

Silver has been recommended by many investigators for use with the corrosive acetic acid. Since many organic compounds of silver are colorless, any slight contamination by silver will produce no objectionable color changes. Tubular or coil-type silver condensers have proved highly successful; in addition to its corrosion resistance, the high heat transfer of silver, allowing the use of smaller condensers, has made its use widespread.<sup>4</sup> Silver condensing tubes have been widely used in Europe.<sup>5</sup> Condensing coils in contact with acetic acid of all strengths for a period of fifteen years have shown no deterioration. Nowack and Spanner<sup>6</sup> state that fine silver is stable at every concentration and that an excess of oxygen has no effect upon its corrosion rate or on that of many solid-solution silver alloys. Forstner<sup>7</sup> states that acetic acid does



not attack silver. Silver is recommended as a corrosion-resistant material by McDonald,<sup>1</sup> and by Roetheli and Forrest.<sup>8</sup> McBride<sup>9</sup> states that silver distillation apparatus is used in the refining of acetic acid resulting from the dry distillation of wood. Ritter<sup>10</sup> recommends the use of silver for concentrated solutions at high temperatures. Lea<sup>11</sup> has reported that pure silver is insoluble in pure acetic acid free from any oxidizing agents. Salkowsky<sup>12</sup> and Watts and Whipple<sup>13</sup> have shown that the presence of oxidizing agents will increase the corrosion rate considerably. Experiments at the National Bureau of Standards<sup>14</sup> showed that a strip of silver (999.3 fine) had a corrosion loss of 1.19 milligrams per square centimeter when immersed in boiling glacial acetic acid for 27 hours.

Tests were conducted at Lehigh University in which silver, nickel, and aluminum were subjected to corrosion by boiling glacial acetic acid in the test procedure previously described. The corrosion data are given in Table 1.

The data presented in Table 1 indicate that silver is superior to both nickel and aluminum with respect to attack by boiling acetic acid. Silver has a smaller weight loss than either nickel or aluminum and does not form a precipitate upon refluxing for a long time; the slight silver solubility produces only a minimum of color change. Nickel, however, causes the precipitation of a considerable amount of black matter, some of which loosely adheres to the metal sample, and the solution is colored green. Aluminum forms a non-adherent film on its surface which may protect the metal for a time; however, after a few hours of refluxing, a voluminous white precipitate results and the solution becomes yellow in color.

**Acetic Anhydride.**—Silver is not attacked during the dehydration of acetic acid to form acetic anhydride. Silver-lined vats have been successfully used in handling acetic anhydride.<sup>14</sup>

**Acetone.**—Acetone does not attack silver. Methyl acetone is the commercial spirit in which methyl acetate and several aldehydes are combined with acetone. Highly purified methyl acetone is successfully produced by the use of silver condensers in the refining of crude methanol.<sup>9</sup>

**Acetylsalicylic Acid.**—The corrosion resistance of silver in acetylsalicylic acid is satisfactory.<sup>15</sup>

**Acetylene.**—Silver is rapidly attacked at 600 °C, forming an explosive compound.<sup>10</sup>

**Alkali Cyanides.**—Silver is attacked by all alkali cyanides either fused or in solution.<sup>10</sup> See also under other headings.

**Alkali Sulfides.**—Silver is rapidly attacked and discolored.<sup>2, 16</sup>

**Alum.**—Silver has been found to be unattacked by alum used in the dyestuff plant.<sup>2</sup>

**Aluminum Sulfate.**—Stainless steel and nickel-chromium alloys have been found to be attacked by hot solutions of aluminum sulfate.<sup>3</sup> Silver has been found to be unattacked by the aluminum sulfate used in a dye-stuff plant.<sup>2</sup>

**Ammonia.**—Silver is not attacked at 20 °C by an oxygen-free aqueous solution. However, at elevated temperatures ammonia gas attacks silver readily<sup>10</sup> with resulting decomposition of ammonia. Nowack and Spanner<sup>6</sup> and Beilby and Henderson<sup>17</sup> state that an unstable nitride is formed at high temperatures, *i.e.*, 600-800 °C, the silver assuming a spongy appearance.

**Ammonium Carbonate.**—Silver is not attacked.<sup>6</sup>

**Ammonium Chloride.**—The attack of ammonium chloride vapor on silver is forty times greater than that of hydrogen chloride.<sup>6</sup> In aqueous solutions a silver chloride layer is formed. Tupholme<sup>2</sup> states that silver is unattacked by a cold ammonium chloride solution in a dyestuff plant, but that a very slight attack has been observed by the solution when boiling in air. Ritter<sup>10</sup> states that silver is sharply attacked by both solution and vapor of ammonium chloride. Of the twenty-one metals tested by Hatfield, all of the common metals except Nichrome were attacked.<sup>3</sup>

**Ammonium Hydroxide.**—Silver is not attacked, according to Nowack and Spanner<sup>6</sup> and Ritter<sup>10</sup> at room temperature (20 °C) by an oxygen-free aqueous solution. Rogers, Schoonover, and Jordan<sup>14</sup> state that silver is only slightly attacked.

**Ammonium Hydroxide-Chloride Mixture.**—Silver is rapidly attacked.<sup>14</sup>

**Ammonium Polysulfide.**—Solutions of ammonium polysulfide form an adherent layer of silver sulfide.<sup>6</sup>

**Ammonium Sulfate + 5% Sulfuric Acid.**—Silver has been found to be unattacked.<sup>2</sup>

**Aniline Dyes.**—Silver equipment has been successfully used in the preparation of aniline dyes and dyestuffs.<sup>14</sup>

**Aqua Regia.**—Aqua regia is a mixture of hydrochloric acid and nitric acid in a ratio of 3 to 1. The solution usually contains nitrosyl chloride and free chlorine. Gold and platinum are soluble in aqua regia, whereas silver and silver-rich gold alloys undergo little attack even in a heated solution.<sup>6</sup> Initial attack results in the formation of a protective silver chloride film.<sup>6, 7</sup>

**Arsenic Acid.**—Arsenic acid attacks silver<sup>10</sup> under some conditions.

**Artificial Silk Industry.**—See Acetate Rayon.

**Atmosphere.**—Exposure to pure dry or moist air has no effect on silver. Dry or moist oxygen at ordinary temperatures and pressures does not attack silver. Oxidation and tarnishing of silver in air are discussed in Chapter 6, and later in this chapter.

**Barium Peroxide.**—Silver is attacked by barium peroxide.<sup>18</sup>

**Benzaldehyde.**—Benzaldehyde attacks silver at 50 °C.<sup>6, 10</sup>

**Benzoic Acid.**—Vacuum pans, evaporators, condensers, and storage vats made or lined with fine silver have been employed in the production of benzoic acid.<sup>5, 19</sup>

**Beverages.**—Silver pipe lines, siphons, tops, nozzles, and containers have long been used for handling and dispensing beverages.<sup>5, 14</sup> Silver-lined containers have especial value in the beer industry since long storage in contact with silver causes neither discoloration nor change in flavor. In general, silver is stable to all beverages which contain no sulfur.<sup>7</sup>

Sterling silver cooling coils have been used for fruit syrups, especially where a slight contamination or discoloration would occur if copper, nickel, or some other metal were used.<sup>19</sup> Sterling silver was used in preference to the pure metal because of the lower strength of the pure silver. See also **Brewery Fluids**.

**Bismuth Oxide.**—Silver is but very slightly attacked by bismuth oxide.<sup>18</sup>

**Bleaching Powder.**—Bleaching powder attacks silver readily.<sup>2</sup>

**Borax, Fused.**—Silver is dissolved by fused borax (sodium tetraborate).<sup>7, 18</sup>

**Boric Acid.**—The use of silver in a dyestuff plant has shown that it is not attacked by boric acid.<sup>2</sup>

**Brewery Fluids.**—Nowack and Spanner<sup>6</sup> state that there is a critical point in the minute solution of silver ions below which there is a stimulation of the growth of certain bacteria; therefore, they state that the possibility exists that organic fermentation may be influenced in a favorable direction by a minute solution of silver ions.

Silver valve disks are employed for special fittings in the brewery department of many plants. An important factor in the beverage industry which favors the use of silver is the ease with which the surface of silver containers can be kept free from bacteria.<sup>19</sup> See also under **Beverages**.

**Bromic Acid.**—Silver undergoes slight attack<sup>18</sup> and is not recommended for use in contact with bromic acid.<sup>10</sup>

**Bromine.**—Bromine attacks silver slowly at ordinary temperatures; the attack becomes smaller upon the formation of a protective film of AgBr. Bromine attacks silver to a greater extent than chlorine, the attack increasing in the presence of moisture.<sup>2, 6, 14</sup> Fine silver, therefore has only a limited application with bromine; certain high-silver alloys may be useful in this field, however.<sup>10, 14</sup>

**Bromine-Vapor Mixtures.**—Silver is severely attacked by bromine vapor in the presence of moisture.

**Calcium Carbonate.**—Silver is but very slightly attacked by CaCO<sub>3</sub>.<sup>18</sup>

**Carbolic Acid.**—See **Phenol**.

**Carbon Dioxide.**—Silver is stable in carbon dioxide at ordinary temperatures.<sup>7</sup>

**Carbon Disulfide.**—Nowack and Spanner,<sup>6</sup> Krais,<sup>21</sup> Ritter,<sup>10</sup> and Stahler<sup>18</sup> state that carbon disulfide vapor does not attack silver. However, Forstner<sup>7</sup> states that silver is attacked.

**Carbon Monoxide.**—Forstner<sup>7</sup> states that carbon monoxide attacks silver at 300°C to form silver oxide. Berthelot<sup>22</sup> reports that at 300 °C carbon is precipitated and a simultaneous disintegration of silver takes place. He believes that this is a consequence of the beginning of the formation of a compound analogous to iron carbonyl.

**Carbon Tetrachloride.**—Tupholme<sup>2</sup> states that carbon tetrachloride does not attack silver.

**Carbonates.**—Silver is stable to all alkali-metal carbonates.<sup>6</sup>

**Carbonic Acid.**—Silver is stable in carbonic acid at ordinary temperature.<sup>7, 18</sup>

**Cesium Hydroxide.**—The attack of cesium hydroxide is perceptible only near 500 °C.<sup>20</sup> See also **Sodium Hydroxide**.

**Chloracetic Acid.**—The affinity of chloracetic acid for silver increases rapidly with increasing dilution, whereas that of hydrochloric acid undergoes but a slight increase.<sup>23</sup>

**p-Chlorbenzaldehyde.**—p-Chlorbenzaldehyde attacks silver at 50 °C.<sup>6</sup>

**Chlorates (Alkali Metals).**—Nowack and Spanner<sup>6</sup> state that the presence of chlorates in hydroxide fusions results in rapid attack upon silver.

**Chloric Acid.**—Silver reacts readily with chloric acid to form silver chloride and silver chlorate.<sup>6, 10, 18, 24</sup> Chloric acid oxidizes large quantities of finely divided silver.<sup>25</sup>

**Chlorine.**—Dry chlorine attacks silver to a slight extent at ordinary temperatures;<sup>26</sup> heating accelerates the attack.<sup>7</sup> However, although dry chlorine will initially attack silver, a protective silver chloride film is immediately formed on the surface of the metal and the attack ceases. Traces of moisture, however, will destroy the protective film and lead to a progressive attack.<sup>6</sup> Silver apparatus has been satisfactory in many operations in the presence of chlorine. The handling of chlorine, wet or dry, in silver is fairly common practice in filtration plants employing chlorination.<sup>14</sup> Although silver has only limited application in many respects, several high-silver alloys may be applicable.

**Chlorine-Vapor Mixture.**—Silver is severely attacked by chlorine vapor in the presence of moisture.<sup>14</sup>

**Chromic Acid.**—Silver is readily attacked by chromic acid with the formation of a loosely adherent layer of red silver chromate.<sup>6</sup>

**Cider.**—The widespread use of silver in the cider and brewing indus-

tries in the form of siphons, pipe lines, pasteurizing coils, and nozzles for filling machines, shows that the metal is completely inert to these liquids.<sup>1</sup>

**Citric Acid.**—Silver is not attacked by citric acid.<sup>7, 16</sup>

**Coal-tar Products.**—Silver condensers are used in the preparation of certain coal-tar products.<sup>14</sup>

**Copper Oxide.**—Silver is not attacked at the higher temperatures.<sup>10</sup>

**Cupric Chloride.**—Tupholme<sup>2</sup> states that silver has been used in dyestuff plants and that it is unattacked by cold solution of cupric chloride. In the boiling solution, however, silver is attacked. Nowack and Spanner<sup>6</sup> state that silver is attacked only by the hot solution.

**Cupric Nitrate.**—Ritter<sup>10</sup> and Lea<sup>27</sup> state that a neutral solution of copper nitrate does not attack silver. Stahler<sup>18</sup> and Lea<sup>27</sup> report that copper nitrate does not react even with finely divided silver.<sup>10</sup>

**Cupric Sulfate.**—Silver is recommended for use with copper sulfate solution.<sup>10</sup>

**Cupric Sulfate-Sulfuric Acid Solution.**—Silver is unattacked by a solution of 10 per cent copper sulfate and 2 per cent  $H_2SO_4$ ; this is a solution that is used in dyestuff plants.<sup>2</sup>

**Cuprous Chloride.**—At high temperatures silver is attacked by cuprous chloride.<sup>7</sup> Lea<sup>27</sup> states that the photochloride is formed.

**Cuprous Nitrate.**—Silver is attacked by cuprous nitrate solutions at high temperatures.<sup>7</sup>

**Cuprous Sulfate.**—Cuprous sulfate solutions at elevated temperatures attack silver.<sup>7</sup>

**Cyanogen.**—Silver is not attacked by cyanogen at any temperature.<sup>18</sup>

**Dairy Products.**—Silver-plated cooling coils are in common use.<sup>15</sup>

**Dyestuffs.**—Tupholme<sup>2</sup> has indicated that silver equipment has found considerable application in solving the corrosion problems of dyestuffs plants. For the resistance of silver to the many chemicals employed see under individual headings.

Silver equipment has been used in the manufacture of aniline dyes and dyestuffs.<sup>14</sup>

**Essential Oils.**—Silver equipment has been successfully used in handling essential oils.<sup>14</sup> A valuable characteristic of silver is that derived from the absence of catalytic effects which might cause the decomposition of essential oils that are so necessary for the characteristic flavors of many products.<sup>19</sup> Distillers of essential oils use silver-lined pans, coils, and taps.<sup>15</sup>

**Ether (Ethyl).**—Silver is unattacked by ethyl ether.<sup>2</sup>

**Ethyl Chloride.**—Tupholme,<sup>2</sup> in discussing equipment used in dyestuff plants, states that ethyl chloride does not attack silver.

**Fatty Acids.**—Considerable usage of silver equipment has shown that silver is unattacked by fatty acids.<sup>2, 7, 18, 28</sup> The presence of strong

oxidizing agents will cause slight corrosion. Silver is resistant to stearic, oleic, palmitic, and other fatty acids<sup>2, 6, 7, 10</sup> and silver equipment has found considerable use even at the high temperatures and pressures encountered in the fatty-acid industry.<sup>7, 10</sup> According to Stahler,<sup>18</sup> only in presence of excess dissolved oxygen is there a possible reaction.

Zinc, sodium, magnesium, aluminum, iron, and tin react with saturated fatty acids at 350 °C to form carbon dioxide, water, hydrogen, and hydrocarbons of the olefin series. Copper, silver, and the heavy metals do not cause this decomposition. The same decomposition takes place with the unsaturated acids.<sup>29</sup>

**Ferric Alum.**—A solution of ferric alum readily dissolves silver at ordinary temperatures with the production of a ferrous salt, and if the ferric compound is in excess, all of the silver is dissolved.<sup>27</sup>

**Ferric Ammonium Alum.**—A large excess of finely divided silver, upon standing for several days in a ferric ammonium alum solution with frequent agitation, was observed by Lea<sup>27</sup> to cause considerable discoloration of the solution. The reducing action of the silver on ferric salts is limited and ceases before the reaction is complete.

**Ferric Oxide.**—Silver is but very slightly attacked by ferric oxide.<sup>18</sup>

**Ferric Sulfate.**—At the boiling point of the solution, silver reacts, forming silver sulfate and ferrous sulfate. Upon cooling, metallic silver is precipitated.<sup>6, 7, 18</sup>

**Ferrous Ammonium Sulfate.**—Silver is attacked by ferrous ammonium sulfate on heating.<sup>6</sup>

**Ferrous Sulfate.**—Silver is attacked by ferrous sulfate on heating.<sup>6, 7</sup>

**Fluorides.**—Although attacked to a slight extent by some fluoride fluxes, the attack is less serious with silver than with other metals. Many testing procedures require the use of silver crucibles.<sup>15</sup> Silver-lined stainless steel pipes are used to carry boron trifluoride which is used in the synthesis of urea. Boron trifluoride attacks steel readily.<sup>15</sup>

**Fluorine.**—As with the other halides, a protective silver fluoride coating is formed on silver when in contact with fluorine gas. Ebert, Rodowskas, and Fraser<sup>30</sup> report that at 300 °C a black substance quite different from AgF is formed; they suggest the formation of AgF<sub>2</sub>. Above 450 °C only AgF is formed. Silver is only slightly coated with AgF upon heating in dry fluorine.<sup>31</sup> Ritter<sup>10</sup> recommends the use of silver with fluorine and says that there is but a very slight attack upon silver at room temperature (20 °C).

**Foodstuffs.**—In the production of foodstuffs, silver has been used with much success; silver is stable and is unattacked by almost all of the common foods with the exception of those containing sulfur. The food industries use silver in preference to other metals in many applications, especially where a slight contamination or discoloration would

occur if copper, nickel or some other metal were used.<sup>19</sup> Silver has been highly recommended by many investigators.<sup>6, 7, 10, 14, 32</sup>

**Formaldehyde.**—The wide use of silver in industry for handling formaldehyde is an indication of its high resistance to the attack of this chemical. The use of formaldehyde in the manufacture of pharmaceuticals and the various formaldehyde resins requires a chemical of the highest purity and freedom from contamination. Silver-lined containers have replaced rubber-lined containers in many instances.<sup>15</sup> The dye-stuff industry has made considerable use of the resistance of silver to formaldehyde.<sup>2</sup>

**Formic Acid.**—Silver has excellent resistance to attack by formic acid;<sup>16</sup> it has been successfully used in many operations in dyestuffs plants.<sup>2</sup>

**Fruit Juices and Extracts.**—Silver is an excellent material for handling fruit juices and extracts. Pure silver and silver-lined stills, condensers, and pipe lines are in successful use. Silver is most useful where strict color and flavor standards are encountered.<sup>7, 14, 19</sup>

**Gelatin.**—Gelatins do not attack silver.<sup>7</sup>

**Glass (molten).**—Silver is soluble in molten glass.<sup>18</sup>

**Glue.**—Silver is unattacked by ordinary glue.<sup>7</sup>

**Glycerin.**—Silver is not attacked by glycerin. Silver-lined steel barrels have found considerable use in transporting pharmaceutical glycerin.<sup>14</sup>

**Halogen Gases.**—In general, the resistance of silver to dry halogen gases at room temperature is good, protection being afforded by an inert protective halide film. Increased temperature and presence of water increase attack. Bromine and iodine attack silver to a greater extent than chlorine. Fluorine has only a very slight action on silver and then only at temperatures greater than 300 °C.<sup>6</sup>

**Hydriodic Acid.**—Silver is readily attacked by hydriodic acid as long as the possibility of halogen formation exists.<sup>6</sup>

**Hydrobromic Acid.**—Silver is easily attacked by hydrobromic acid with the formation of adherent silver bromide layers which tend to lessen the progressive attack of the hydrobromic acid.<sup>7</sup> Silver is, however, considerably attacked by all concentrations.<sup>16</sup>

**Hydrochloric Acid.**—The corrosive attack of hydrochloric acid upon silver has been investigated extensively. It is generally agreed at the present time that silver is attacked to some degree by all concentrations of acid; however, the initial attack results in the formation of a film of silver chloride which has a different behavior toward the acid than the original sample of pure silver. In dilute acid solutions this film, which has good adherence, is insoluble. With increasing concentrations of acid and increasing temperatures, solution of the silver chloride is favored. Agitation and abrasion of the silver chloride are contributing

factors to its solution. Therefore, a silver-lined object will not be attacked progressively, since in certain solutions the silver chloride may furnish complete protection. The effectiveness of the film depends upon existing conditions.

A noteworthy investigation of the attack of hydrochloric acid on silver was carried on by Nowack and Spanner,<sup>6</sup> who investigated the corrosion of silver and several silver alloys by various concentrations of hydrochloric acid. These investigators immersed several metal samples in normal hydrochloric acid at room temperature for a period of three months. Pure silver, a silver-copper-cadmium alloy, a silver-cadmium-thallium alloy, and a silver-manganese-aluminum alloy showed no weight losses. The weight changes observed were gains of from 56 to 380 milligrams per square decimeter. The corroding solutions were colorless, and there was no alteration of the acid.

In Table 2 a summary is given of the results of experiments performed by Nowack and Spanner. Metal samples were alternately immersed and then raised out of 1N, 2N, and 3N hydrochloric acid solutions. The acid solutions were held at 35 °C for one week.

Table 2.—Weight Losses (mg per sq cm).

Metal	1N HCl Weight Loss	2N HCl Weight Loss	3N HCl Appearance of Acid
100% Ag	0.0	0.2	colorless
98% Ag, 2% Pd	.10	.3	—
93.5% Ag, 6.5% Cu	+.60	+.5	greenish yellow
93.5% Ag, 2.5% Cu, 4% Cd	+.90	+1.0	greenish yellow
89% Ag, 10% Mn, 1% Al	.30	.5	colorless

The resistance of fine silver and several silver alloys to 20-per cent hydrochloric acid was also investigated. Nowack and Spanner's results, secured over a period of 361 hours in which fresh acid was used every 48 hours, showed that several solid-solution alloys had practically the same stability as fine silver, whereas the alloys of heterogeneous structure underwent considerably higher weight losses.

In 20-per cent hydrochloric acid at 100 °C for 40 hours, the silver-palladium and the silver-copper-zinc-nickel alloys underwent considerable attack. An alloy of 83.5 per cent silver and 16.5 per cent copper gave favorable results.

Saturation of 20-per cent hydrochloric acid at 100 °C with oxygen gas revealed an increased attack upon immersed samples. As in all of the preceding cases, fine silver was more stable than the silver alloys, the solid-solution alloys more nearly approximating the fine silver.

McDonald<sup>28</sup> states that hydrochloric acid attacks silver slowly at a rate depending on the temperature and on the presence or absence of oxidizing agents. The latter, if present, are favorable to the production of nascent chlorine. McDonald recommends the use of silver for han-



ding dilute hydrochloric acid provided the silver chloride film, formed as a result of the initial attack, is not removed.

Rabald<sup>32</sup> found that silver is but slightly attacked by either cold dilute or cold concentrated hydrochloric acid. According to Rabald, 15-per cent acid under pressure at 150 °C completely destroyed silver, whereas under ordinary conditions at 25 °C a layer of 0.026 mm of silver

Table 3.—Weight Changes (+ = gain).

Length of Test (hrs)	Atmosphere	A (HCl vapor) (%)	B (liquid-vapor junction) (%)	C (Boiling F solution) (%)
Concentrated Hydrochloric Acid (sp. gr. 1.19)				
<i>Silver</i>				
0-24	air	+ 0.10	2.50	1.00
	Without O <sub>2</sub>	.02	.85	.50
	Excess O <sub>2</sub>	.75	5.00	1.70
	Excess N <sub>2</sub>	.50	4.75	.40
24-48	air	0.50	5.00	+ 2.00
	Without O <sub>2</sub>	.00	.50	+ 0.50
	Excess N <sub>2</sub>	.10	5.00	+ 0.80
<i>Hastelloy B</i>				
0-24	air	0.05		0.30
24-96	air	.50		1.00
96-216	air	.60		2.00
216-288	air	.80		3.80
<i>Monel</i>				
0-29	air	1.50	75.00	84.00
<i>Nickel</i>				
0-24	air		39.00	87.50
<i>Copper</i>				
0-24	air	3.00	24.00	15.00
24-48	air	3.20	50.0	45.00
30% (by vol.) Hydrochloric Acid (conc. HCl diluted with 70% water)				
<i>Silver</i>				
0-24	air	0.03	0.50	0.35
24-96	air	.10	1.00	.80
<i>Copper</i>				
0-24	air	0.00	2.20	3.00
24-96	air	.50	5.60	6.50

was removed in one month. Excess oxygen was found to favor the attack. Hofmann and Hofmann<sup>33</sup> report that their experiments showed atmospheric oxygen to be a more important factor in the oxidation of silver than the literature leads one to believe. They immersed a 78-square centimeter sample of the purest silver foil in 300 ml of 20-per

cent hydrochloric acid, open to the air, and found that the amount of dissolved silver was equivalent to 0.32 gram of silver chloride in 20 days.

Prout found that silver chloride is superficially attacked by hydrochloric acid and that a small portion dissolves. Lea,<sup>27</sup> however, states that hydrochloric acid of specific gravity of 1.20 has absolutely no effect upon silver. The more recent theory concerning hydrochloric acid attack is not in agreement with Lea's statement.

The present authors observed the attack of several concentrations of hydrochloric acid under various conditions upon silver, Hastelloy B, Monel, and nickel.

On the basis of the results secured, it was concluded, as had been shown previously by other investigators, that the chemical attack of silver is dependent upon the protective nature of the silver chloride film formed upon initial attack. The tests were conducted according to the standardized test procedure described on a prior page. The attack on the silver, or rather the solution of the silver chloride protective film, is most critical when the sample is only partially immersed.

Table 3 lists the weight changes of metal samples that result from the attack of boiling hydrochloric acid.

In general, the weight loss of a totally immersed sample in concentrated hydrochloric acid was less than 1 per cent whereas the weight loss of the partially immersed sample varied between 0.50 and 5.00 per cent. The partially immersed samples were more sensitive to the presence of oxygen than were the totally immersed samples. A concentrated hydrochloric acid solution saturated with oxygen by bubbling oxygen gas into the boiling solution gave slightly higher corrosion rates than those which resulted when the test was performed under ordinary atmospheres. Tests made in atmospheres containing an excess of nitrogen, and others where oxygen was removed by alkaline pyrogallol, gave minimum corrosion rates.

The protective properties of thin silver chloride films on a silver sample were observed in the vapor of boiling hydrochloric acid. The silver chloride coatings were produced by partially immersing pieces of silver in concentrated hydrochloric acid and in concentrated hydrochloric acid diluted with 70 per cent by volume of water at 50 °C for periods of one and three weeks. The weight changes noted were as follows:

Sample No.	Corrosive Material	Temp. (°C)	Length of Test	-Weight (%)	... (mdd)
J-1	Concentrated HCl	50	3 weeks	2.20	2.60
J-3	HCl used in J-1	50	1 week	+ 0.10	+ 0.34
J-5	Concentrated HCl	50	1 week	1.01	3.51
J-2	30% HCl (by volume)	50	3 weeks	0.26	0.31
J-4	HCl used in J-2	50	1 week	+ 0.18	+ 0.53
J-6	30% HCl (by volume)	50	1 week	0.49	1.70

From the above data it may be inferred that even in contact with concentrated hydrochloric acid, the silver chloride coating becomes protective after a time. Sample J-3 was immersed in the same solution as was used in J-1, and no loss was observed. In a control sample, J-5, hydrochloric acid of the same strength, but which had not been contaminated by any silver chloride solution, showed that a progressive attack had taken place over a one-week period. It seems reasonable to assume that this solution would act similarly to that used in J-1. Similar behavior was observed with the dilute hydrochloric acid (30 per cent by volume).

Physical inspection of the above samples revealed a silver chloride film only on the immersed or C part of the metal specimen. It is assumed that there was little or no silver chloride on the A part, which was not immersed. The C and A samples were compared by placing the samples in the vapor of boiling concentrated hydrochloric acid for five days. The weight losses are as follows: (+ = gain)

Concentrated HCl		Dilute HCl (30% by vol.)	
Sample	C part (%)	Sample	C part (%)
J-1	+2.46	J-2	+0.74
J-2	+0.74	J-4	+1.47
J-3	+0.53	J-6	+0.65
J-4	+1.47		
J-5	+1.90		
J-6	+0.65		

As is evidenced in the preceding discussions, the use of silver with hydrochloric acid is subject to the action of many variables. It is definitely known, however, that considerable use of silver equipment has been made in installations for processes in which dilute hydrochloric acid is one of the products. The handling of both wet and dry chlorine in silver is fairly common practice in filtration plants employing chlorination.<sup>34</sup>

**Hydrofluoric Acid (aqueous).**—Silver has excellent resistance to attack by the water solution of hydrogen fluoride, and it has found widespread use in industry. It has been stated by some investigators<sup>7</sup> that silver is slightly attacked by the acid; however, on the basis of tests made by the writers and upon recent independent investigations, it has been concluded that the hydrofluoric acid does not attack silver. If, however, fluosilicic acid is present, a slight attack will be noted; also, according to Stahler,<sup>18</sup> a reaction is possible only in the presence of dissolved oxygen. After immersion in the 48-per cent chemically pure grade of aqueous hydrofluoric acid at room temperature for a period of 9 weeks, a sample

of 999 fine silver,  $5 \times 5 \times .0051$  cm, was observed by the writers to have gained 0.09 per cent in weight. There were no visible signs of attack or of film formation on the silver sample.

**Hydrogen.**—Silver forms a hydride, but only upon the action of atomic hydrogen. Hydrogen, under normal conditions, is not reactive with silver. The silver hydride is stable in air up to  $500^{\circ}\text{C}$ ; above  $500^{\circ}\text{C}$  the hydride is volatile.<sup>6</sup>

**Hydrogen Chloride.**—According to Stahler,<sup>18</sup> above  $150^{\circ}\text{C}$  silver is easily attacked by hydrogen chloride gas. For the authors' test results and additional references, see **Hydrochloric Acid**.

**Hydrogen Peroxide.**—Silver acts as a catalyst in decomposing hydrogen peroxide with the formation of a gray-white film upon the surface of the silver. A soluble hydrated oxide is the final result. The surface of the silver is etched.<sup>6</sup>

**Hydrogen Selenide.**—Silver is easily attacked by hydrogen selenide.<sup>18</sup>

**Hydrogen Sulfide.**—Silver is readily attacked by hydrogen sulfide with the formation of a black silver sulfide deposit. See also section on Tarnishing, at the end of this chapter.

**Hypochlorous Acid.**—Acid is readily attacked by hypochlorous acid.<sup>18</sup>

**Ink.**—Silver has no reaction with the common inks, and silver vessels are often employed in their preparation.<sup>14</sup>

**Iodic Acid.**—Silver is readily attacked by iodic acid.<sup>18</sup> Iodic acid is capable of oxidizing large quantities of finely divided silver.<sup>25</sup>

**Iodine Solution.**—As used in dyestuff plants, silver has been found to be unattacked.<sup>2</sup> Matignon<sup>35</sup> states that iodine placed on thin sheets of silver gradually converts the whole of the metal into the iodide at ordinary temperatures. Ritter<sup>10</sup> reports that there is a sharp attack on silver by iodine solution at  $20^{\circ}\text{C}$ .

**Iodine in Potassium Iodide.**—Tupholme<sup>2</sup> states that silver is readily attacked by a solution of iodine in potassium iodide.

**Iron Oxide.**—It has been reported<sup>18</sup> that iron oxide ( $\text{Fe}_2\text{O}_3$ ) does not attack silver at all, or at most very slightly. Ritter<sup>10</sup> recommends silver for use in contact with  $\text{FeO}$  at elevated temperature.

**Iron Sulfate.**—Ritter<sup>10</sup> reports that silver is attacked by  $\text{FeSO}_4$  solution.

**Jellies.**—In the production of foodstuffs, silver has been used more widely abroad than in this country. Jams, jellies and allied products are made in pure silver and silver-lined autoclaves, evaporating pans, vacuum stills and similar equipment.<sup>14</sup> See also **Foodstuffs**.

**Lactic Acid.**—Tupholme<sup>2</sup> reports that silver is not attacked by lactic acid. An experiment at the National Bureau of Standards, Washington, D. C.,<sup>14</sup> showed that a strip of silver (99.993 per cent) having a surface area of 6.8 square centimeters lost 0.011 gram when immersed in a 50 per cent solution of lactic acid (by volume) and boiled under a reflux condenser for 26 hours.

**Lead Oxide.**—Information concerning the effect of lead oxide upon silver is contradictory. Stahler,<sup>18</sup> in an early work, reports that there is an appreciable attack upon silver by lead oxide. It is reported by Ritter<sup>10</sup> that there is a sharp attack at high temperatures. Forstner,<sup>7</sup> on the other hand, states that lead oxide does not attack silver very greatly even at high temperatures.

**Lead Peroxide.**—There is an appreciable attack upon silver by lead peroxide.<sup>18</sup>

**Magnesium Chloride.**—Silver under the conditions of use in dyestuff plant is not attacked by magnesium chloride.<sup>2</sup>

**Magnesium Sulfate.**—According to Tupholme,<sup>2</sup> silver is not attacked by magnesium sulfate as used in the dyestuff industry.

**Malic Acid.**—Silver is very resistant to fatty acids. It is useful as a coating even at high temperatures and pressures in the fatty acid industry.<sup>7</sup>

**Mercuric Chloride.**—Mercuric chloride is reduced by silver, as is the iodide.<sup>18</sup> Silver is not recommended for use with mercuric chloride.<sup>10</sup>

**Mercurous Chloride.**—Silver is not recommended, since it readily reduces mercurous chloride.<sup>10, 18</sup>

**Mercuric Iodide.**—Mercuric iodide is reduced by silver.<sup>18</sup>

**Mercury.**—Silver, because of the ease with which it amalgamates with mercury, cannot be satisfactorily used in contact with that metal.<sup>6</sup>

**Mine Waters.**—Acid mine waters are extremely corrosive; a precious metal is said to be required to resist them completely. Stainless steel, Monel, and Cor-Ten are attacked.<sup>15</sup>

**Nitrate Fusions.**—Silver is attacked by nitrate fusions, with formation of silver nitrate.<sup>6</sup>

**Nitric Acid.**—Silver, as indicated by the reports of several investigators,<sup>6, 10, 18</sup> is readily attacked by nitric acid. The observations of Stansbie<sup>36</sup> indicate, however, that the metal is not dissolved unless the temperature and concentration of the solution are such that nitrate or nitrous acid is decomposed with evolution of gas. The results of experiments carried on by Stansbie indicate that the presence of nitrous acid accelerates the action of nitric acid on silver, as does an accumulation of nitrite near the surface of the dissolving metal. Nowack and Spanner<sup>6</sup> report the solution of silver by nitric acid with nitric oxide formation, the nitric oxide hastening the process. A hundredth of a gram of hydrazine or sodium azide in 20 cubic meters of 8*N*, or stronger, nitric acid prevents the dissolving of silver for several days by decomposing the  $\text{HNO}_2$ , which acts as an accelerator. At the boiling point the addition is effective in 3*N* acid for some hours.

**Nitric-Sulfuric Acids.**—Silver is attacked by mixtures of nitric and sulfuric acids.<sup>2</sup>

**Nitric Oxide.**—Although Stahler<sup>18</sup> and Ritter<sup>10</sup> report that there is

no attack upon silver by nitric oxide, Forstner,<sup>7</sup> in a more recent work, reports that the metal is attacked.

**Nitrogen.**—The results of several investigations indicate that there is no reaction between silver and nitrogen. Silver heated to 500 °C in a sealed tube with nitrogen was not affected.<sup>18</sup>

**Nitrogen Tetroxide.**—Nitrogen tetroxide in contact with silver forms silver nitrate, which decomposes on heating.<sup>7</sup>

**Nitrosyl Chloride.**—Sudborough,<sup>37</sup> in a study of the action of nitrosyl chloride on metals, found that there was no action between that chemical and silver in the cold. At 100 °C the metal became coated with a film of silver chloride which prevented further action, and even after heating for three days this film was the only sign of any action having taken place. Ritter<sup>10</sup> and Forstner<sup>7</sup> also report a slight attack of the silver, but the temperature at which this attack was evident is not recorded.

**Oleic Acid.**—Silver is not attacked by oleic acid.<sup>2</sup> See also **Fatty Acids.**

**Organic Acids.**—Nowack and Spanner<sup>6</sup> state that the noble metals are attacked by organic substances only in exceptional cases. There is very little literature concerning the effect of many of the organic substances upon silver, but the effect of sulfur on silver is well known. For this reason organic acids containing unsaturated sulfur atoms or sulfonic acids should be placed in contact with silver only after a careful investigation of the effects. McBride,<sup>9</sup> in a discussion of practice in hardwood distillation plants, states that silver is commonly used in handling highly refined acid products including methanol, methyl acetone, and allyl alcohol.

**Oxalic Acid.**—Silver is slightly attacked by oxalic acid.<sup>14</sup>

**Oxygen.**—Investigators are quite in accord in statements concerning the resistance of silver to oxygen at ordinary temperature and pressure, but seem to disagree concerning the effect of oxygen on silver at elevated temperatures and pressures. Silver at ordinary temperature is not affected by oxygen.<sup>14, 18</sup> Le Chatelier<sup>38</sup> has observed the formation of black oxide in oxygen atmosphere at 300 °C and 15 atmospheres' pressure. Berthelot,<sup>39</sup> in an investigation in which silver was heated at 500-550 °C in sealed tubes containing dry oxygen, found that the silver was disintegrated and converted into a yellowish-white powder giving the reactions of argentous oxide ( $\text{Ag}_2\text{O}$ ). Similar experiments with dry air gave similar results, and when moist oxygen or air was used the disintegration was more pronounced. The action is appreciable at 200 °C but is not noticeable at 100 °C.

**Ozone.**—Several investigators have noted that either dry or moist ozone forms a black coating on silver.<sup>14, 18, 40</sup> Manchot and Kampshulte<sup>40</sup> state that the black stain is best shown when the metal is heated in a flame and allowed to cool while the ozone impinges on it. The maxi-

num effect is produced between 220 and 240 °C. At higher temperatures the iridescent coloration is less marked, and at 450 °C no change is noticeable. It has been found that minute traces of numerous substances, including oxides of most of the heavy metals and finely divided ruthenium, palladium, and platinum, will cause a blackening at ordinary temperatures.

**Palmitic Acid.**—Silver is completely stable toward hot fatty acids such as stearic and palmitic.<sup>6</sup> See also **Fatty Acids**.

**Pectin.**—Silver has been used satisfactorily in the handling of jellies and gelatins.<sup>7</sup> See also **Foodstuffs, Gelatins**.

**Persulfate Solutions.**—Silver is attacked by persulfates of sodium and potassium. Higson<sup>41</sup> states that persulfates of sodium or potassium convert metallic silver into a peroxide containing more oxygen than corresponds to the formula  $\text{Ag}_2\text{O}_2$ . Because of the smaller solubility of the potassium salt, the reaction is much slower than with the sodium salt. With ammonium persulfate no peroxide is formed, but the ammonium radical is oxidized to nitric acid.

**Pharmaceuticals.**—The resistance of silver or its surface decomposition products to the halogens has made possible the use of silver coatings in the pharmaceutical industry for boiling vessels, heating coils, distillation apparatus, and columns.<sup>7</sup> See also **Phenol**.

**Phenol.**—As indicated in Table 4, the resistance of silver to the chemical attack of phenol has been observed by several investigators.<sup>6, 14, 19, 42, 43, 44</sup> In almost all cases silver has proved itself to be highly resistant to chemical attack.

The rapidly growing demand for synthetic coatings of the phenolic type requires a phenol which is almost free from coloring matter. This is a quality which is sometimes difficult to attain. At lower temperatures, where the phenol is just above its melting point, indefinite standing in silver will produce no discoloration. It is, however, difficult to prevent discoloration of phenol which is at or near its boiling point. Most metals produce considerable change. The presence of silver results in a very small change in color; this is observed only after the phenol has been refluxed continuously beyond 24 hours.

In preparing phenol, especially the high-purity and colorless material required in the production of pharmaceuticals and phenolic resins, silver stills, condensers, and evaporators have found wide acceptance.

The writers have conducted tests in which several metals were compared with respect to their attack by phenol under identical test conditions. All the metals tested were those commonly used wherever high-purity phenol is desired. The metals tested were silver, nickel, 18-8 iron alloy, copper, and aluminum; all were tested in the standard testing procedure as previously outlined.

The weight losses of the metal samples, upon refluxing a 500 ml quantity of phenol, are shown in Table 4.

Table 4.—Weight Losses of Metal Samples in Phenol, Dry and Wet, in mg/sq dm/day.

Metal	Silver		Nickel		18-8 Iron Alloy Wet	Copper Wet	Aluminum Wet
	Dry*	Wet*	Dry	Wet			
0-24 hour test							
Position A	0.0	5.0	+ 12.5	7.5	10.0	7.5	—
B	+ 3.3	4.0	200.0	6.6	3.3	37.0	Dissolved
C	+ 8.2	1.5	0.6	2.0	1.4	4.0	Dissolved
24-96 hour test							
Position A	+ 0.66	1.7	+ 0.33	2.0	0.0	47.2	
B	.22	2.2	17.60	4.1	10.8	24.2	
C	+ .80	13.0	+ 0.15	0.3	0.3	0.0	

\*Wet phenol contains 10 per cent water added to the C.P. dry phenol.

From the standpoint of weight loss, silver, nickel, and 18-8 iron alloy show approximately the same attack. The solution of a very small quantity of metal has a pronounced effect upon the color of the resulting phenol, as well as a tendency to elevate its boiling point. Only upon refluxing wet phenol beyond 24 hours in the presence of silver, nickel, or 18-8, is there a distinct color change in the phenol solution. After 4 days (96 hours) of continuous refluxing in the presence of these metals, the wet phenol which contained the nickel had a wine color; the silver and 18-8 samples caused an amber to black appearance. That the color change was a result of metal solution was shown by the fact that a similar sample of wet phenol not in contact with metal did not change in color when refluxed for the same time. In the colored solutions mentioned above, the solutions could not be clarified by filtration.

The surface condition of the metal sample is of importance. Silver will darken readily in boiling wet phenol, an adherent gray-black film forming on the sample; an abrasive is necessary to remove this film. The nickel, however, is coated with a thin, non-adherent black slime which is easily removed by rubbing with wet cotton. Upon removal of this film the nickel assumes its original appearance.

After 7 days (168 hours) of constant refluxing, the dry phenol had a black color when contaminated with nickel, and only a slight amber color where silver was in contact with the boiling solution. Both silver and nickel had similar weight losses, except for a marked corrosion loss of the partially immersed sample (Position B).

In similarly conducted tests, Schoonover<sup>14</sup> at the National Bureau of Standards found that silver suffered no loss of weight in either vapor, liquid-vapor junction, or in total immersion within the liquid phenol (wet) for a period of 26½ hours. A 3.5-per cent silver-tin alloy lost 3.7 per cent by weight in the boiling liquid, 1.8 per cent at the liquid line and 0.0 per cent in the vapor. Pure tin gave similar results.

At a temperature just above the melting point of phenol, *i.e.*, 50 °C, a sample of dry phenol was not colored by contact with a sheet of silver over a period of 3 weeks. The silver did not change in weight.



This same sample was allowed to remain at room temperature, solidified, and there was no apparent physical change in either the phenol or in the silver sheet after 10 weeks.

Rhodes, Riedel, and Hendricks<sup>42</sup> investigated the corrosion rates of several metals upon attack by tar acids. Their tests were run for about 100 days. Their results are shown in part in Tables 5 and 6.

Table 5.—Weight Losses of Metal Samples in Phenol in mg/sq dm/day.

Metal	Dry Phenol (25 °C)	Wet Phenol (25 °C)	Dry Vapor	Wet Vapors
Aluminum	0.28	0.01	—	1.30
Copper	.92	.23	2.10	5.87
Nickel	.13	.08	1.00	.99
Cr-Ni steel (18-8)	.15	.23	.05	1.30
Silver	.03	.12	1.63	.91

These authors state that their tests were made at 25 °C by immersing the metal specimens in the melted tar acid. However, the results, as indicated for phenol, are probably those of the solidified phenol, since the melting point of pure phenol is 41 °C. In measuring the corrosion rates in the vapor of boiling phenol, the metal was in contact with the hot vapor and hot condensate that had formed on the surface of the metal.

Table 6.—Phenol Discoloration

Metal	Dry Phenol (25 °C)	Wet Phenol (25 °C)	Dry Vapors	Wet Vapors
Aluminum	Red	Slight	Disintegrated	Slight
Copper	Black	Black	Black	Heavy black
Nickel	Red	Red	Red	Red
Cr-Ni steel (18-8)	Light pink	Red	Slight	Slight
Silver	Light pink	Slight	Very slight	Slight

Rhodes and his associates confirmed the results of Seligman and Williams.<sup>44</sup> It was observed that the corrosion rate of certain metals, *i.e.*, aluminum, zinc, and lead, was inhibited by the presence of water. This decreased corrosion probably was due to the formation of secondary reaction products which were protective to the metal. Rhodes stated that the use of copper in phenol stills and containers should be avoided, both from the standpoint of corrosion loss and of discoloration of the phenol. Nickel, 18-8 chrome-nickel steel, and silver appear to be satisfactory.

**Phosphates.**—Silver is used in contact with phosphates especially where metal contamination must be avoided.<sup>15</sup>

**Phosphoric Acid.**—Silver is stable toward dilute phosphoric acid solutions even at relatively high temperatures. Phosphoric acid of densities of 1.262 and 1.581, as well as mixtures of phosphoric and hydrochloric acids, do not attack silver. In the presence of metaphosphoric acid and air, silver is attacked by the acid solution at 200 °C.<sup>6</sup> Con-

concentrated boiling acid attacks silver slowly; 90-per cent acid at 300-400 °C dissolves 4-5 mg/sq cm/hour. In general, phosphoric acid attacks in much the same manner as does sulfuric; however, the phosphoric acid attack is much weaker.<sup>6</sup>

Tests made by the authors indicate that silver is corrosion-resistant to 85 per cent C.P. phosphoric acid at temperatures between 75 and 85 °C. After 96 hours' immersion, the weight loss of a silver sample was negligible.

Unpublished data<sup>16</sup> show that 999.5 fine silver lost about 3 mg/sq cm/day when immersed in 85-per cent phosphoric acid at 112 to 121 °C.

Silver is unattacked by the phosphoric acid used in dyestuff plants.<sup>2</sup>

**Photographic Emulsions.**—The chlorides of the alkali metals dissolve silver, especially in the finely divided form. In the fused condition, silver is corroded by the nitrates, chlorides, bromides, iodides, phosphorus salts, borates, and the bicarbonates of the alkali metals.<sup>7</sup>

**Phthalic Acid.**—Vacuum pans, evaporators, condensers, and storage vats of fine silver or silver-lined have been employed in production of phthalic acid.<sup>19</sup> In the refining of wood chemicals copper equipment is general, but silver is commonly used for highly refined acid products of hardwood distillation.<sup>9</sup>

**Potassium Bromide.**—In general, silver reacts easily with potassium bromide.<sup>18</sup> Ritter<sup>10</sup> states that there is a sharp attack on silver by molten potassium bromide.

**Potassium Chloride.**—Stahler<sup>18</sup> reports that silver reacts easily with potassium chloride, which would be expected from a knowledge of the effect of other halides on silver. Ritter,<sup>10</sup> however, states that there is no attack upon silver by a solution of potassium chloride.

**Potassium Cyanide.**—Silver dissolves in potassium cyanide, forming a complex ion.<sup>6</sup> The addition of oxygen increases the attack of the potassium cyanide on silver.<sup>10</sup>

**Potassium Dichromate.**—Potassium dichromate solutions do not show a visible action on silver.<sup>6</sup>

**Potassium Ferrocyanide.**—Silver is dissolved by potassium ferrocyanide.<sup>18</sup>

**Potassium Hydroxide.**—Ritter<sup>10</sup> reports that silver is not attacked by potassium hydroxide. Stahler<sup>18</sup> states that potassium hydroxide melted in a silver crucible contained no silver, but that the exposed surface of the hydroxide had a slight film of silver oxide, causing a slight discoloration.

Dittmar and Prentice<sup>45</sup> found that the action of fused alkalis upon silver crucibles was easily perceptible, and that the action was greatest in the presence of air. Caustic potash (KOH) was found to be much more active than caustic soda (NaOH). See also **Sodium Hydroxide.**

**Potassium Iodide.**—Silver reacts easily with potassium iodide.<sup>10, 18</sup>

**Potassium Nitrate.**—Silver is strongly oxidized by potassium nitrate,<sup>18</sup> and also by mixtures of potassium nitrate and potassium hydroxide.

**Potassium Permanganate.**—Aqueous potassium permanganate solutions attack silver strongly, even at low concentrations and at ordinary temperatures. According to Stahler,<sup>18</sup> neutral solutions of potassium permanganate will dissolve finely divided silver only after a long time. The presence of dilute sulfuric acid will cause the solution to take place more readily.

**Potassium Peroxide.**—Peroxides of the alkali metals attack all noble metals fairly strongly. With silver, an oxide is formed.<sup>6</sup>

**Potassium Persulfate.**—Silver is not recommended for persulfates of either sodium or potassium.<sup>10</sup> A quick reaction follows the attack of potassium persulfate on silver, with a resulting brown discoloration.<sup>6</sup>

**Potassium Sulfide.**—The alkali sulfides blacken silver by forming silver sulfide. See Tarnishing.

**Propionic Acid.**—Propionic acid is handled in silver containers.<sup>15</sup>

**Pyrosulfuric Acid.**—Silver is severely attacked by pyrosulfuric acid. Divers and Shimidzu<sup>46</sup> report that reduced, spongy silver dropped into the acid warmed barely to its melting point gives a momentary hissing and then dissolves rapidly without further effervescing.

**Rayon.**—See Acetate Rayon.

**Rubidium Hydroxide.**—While silver is not attacked by fused alkalis under usual conditions, fused rubidium hydroxide at high temperatures shows some attack on silver with slight discoloration of the salt.<sup>6</sup> This is similar to attack by fused caustic soda (which see) above 500 °C, but is somewhat greater in amount and takes place at somewhat lower temperature.<sup>18, 20</sup> Rubidium and cesium hydroxides corrode silver more than other alkalis.<sup>7</sup>

**Salicylic Acid.**—Silver is used to line vessels in making salicylic acid.<sup>5</sup>

**Sea Water.**—Beutel and Kutzelnig<sup>47</sup> found silver sheets entirely unchanged after 46 days' immersion in sea water.<sup>6</sup>

**Selenic Acid.**—Silver is dissolved by hot concentrated selenic acid, with evolution of  $\text{SeO}_2$  and formation of  $\text{Ag}_2\text{SeO}_4$ .<sup>6, 18</sup> Since this is analogous to attack by sulfuric acid, it is quite possible that silver would resist attack by weaker solutions. Ritter<sup>10</sup> reports that selenic acid (concentration not stated) attacks silver readily at 20 °C.

**Sodium Bicarbonate.**—Though not corroded by aqueous solutions of sodium bicarbonate, silver is attacked by the fused salt.<sup>7, 10</sup> Heating sodium bicarbonate in a silver dish is said to result in the formation of a silver-sodium alloy.<sup>18, 22</sup>

**Sodium Borate.**—Silver is attacked by fused sodium borate,<sup>7, 10</sup> but not by the salt in solution.

**Sodium Bromide.**—Silver is corroded by fused sodium bromide.<sup>7</sup>

**Sodium Carbonate.**—Aqueous solutions of sodium carbonate have no effect on silver. Fused carbonate does not attack it appreciably under ordinary conditions, but at high temperatures (*e.g.*, 500 °C) corrosion has been observed, though less than in the case of caustic soda under similar circumstances.<sup>6</sup>

**Sodium Chloride.**—Solutions of sodium chloride attack silver slowly.<sup>2, 10</sup> Berthelot found that whereas in potassium chloride solution silver kept its color and luster, a violet coloration appeared on the surface when immersed for some time in sodium chloride solution.<sup>48</sup> Adherent crystals of a double chloride were formed.

De Marchi and Fink at Columbia University tested the corrosion resistance of silver and a large number of silver alloys in a 3-per cent solution of sodium chloride, using an intermittent corrosion machine which alternately immersed the specimens in the solution for 15 minutes and exposed them to the atmosphere for 15 minutes. Results obtained for fine silver and sterling were as follows:

	-Corrosion Loss (mdd per day)-		
	Test A, 1 week	Test A, 3 weeks	Test B, 3 weeks
Fine silver	0.058	0.058	0.46
Sterling silver	.167	.148	.36

In general, the corrosion losses for the other silver alloys were much higher. Details of the test procedure and results for other alloys are summarized in the next section of this chapter.

The solubility of silver chloride in sodium chloride solutions bears on the rate of solution of the metal. Barlow<sup>49</sup> tested the solubility of silver chloride in solutions of 23 grams of sodium chloride in from 100 to 700 ml of water, and at temperatures from 20 to 90 °C. He found a gradually diminishing solubility with increased dilution, but rapidly increasing with rise of temperature. The solubility of silver chloride in sodium chloride is greater than in hydrochloric acid solutions; in the latter the solubility increases with dilution as well as with temperature. In solutions of sodium chloride plus hydrochloric acid, the total solubility of silver chloride was almost exactly the sum of the two separate solubilities.

**Sodium Chloride, Fused.**—In fused sodium chloride, silver is rapidly attacked.<sup>7, 10</sup>

**Sodium Cyanide.**—In the presence of air, sodium cyanide is used to dissolve silver in recovering the metal from ores. Silver is also rapidly attacked by fused cyanide.<sup>10</sup>

**Sodium Ferrocyanide.**—Solutions of this salt dissolve silver.<sup>7</sup>

**Sodium Hydroxide.**—Dittmar<sup>50</sup> states that the attack of sodium hydroxide upon metals is dependent on the formation of peroxides, which then constitute the destructive reagent. Silver, platinum, nickel, and an alloy of 91 per cent silver, 7 per cent gold, and 2 per cent nickel are not

acted upon in the absence of air by corrosive caustic solutions which are usually above 60 per cent of potash (potassium hydroxide) or soda (sodium hydroxide). All of these metals, according to Dittmar, are attacked by fused alkalis in the presence of air; the silver is attacked to the least extent. Dittmar and Prentice<sup>45</sup> report that the action of fused alkalis upon silver crucibles is easily perceptible and that the action is greatest in the presence of air. Caustic potash was found to be much more active than caustic soda.

Le Blanc and Bergman<sup>51</sup> investigated the action of various metals on fused sodium hydroxide at temperatures ranging from 400 to 720 °C in an atmosphere of nitrogen. Gold was found to be the only metal that completely withstood attack by the anhydrous fused caustic. Platinum, copper, iron, nickel, aluminum, zinc, and magnesium cause an evolution of hydrogen. Silver is attacked by sodium hydroxide only above 500 °C upon the evolution of hydrogen. The attack upon silver of rubidium, cesium, and potassium hydroxides is perceptible at lower temperatures.<sup>51</sup>

Silver is not soluble in boiling caustic potash or caustic soda solutions; lead, if present in the silver, will be dissolved.<sup>52</sup> Only in the presence of oxidizing agents is there a perceptible attack upon silver by caustic solutions.<sup>6</sup>

Fusions of sodium and potassium hydroxide in silver crucibles are common in analytical chemistry. Silver evaporating pans, molds, and ladles have been widely used in the preparation of the highest grades of sodium and potassium hydroxide.

The use of caustic soda in the artificial silk and related industries where metallic contamination is very detrimental, together with the growing demand for caustic free from metallic contamination, caused the writers to investigate the attack of molten 70 per cent caustic soda upon silver, nickel, and iron; the latter metals are extensively used at present.

Three crucibles each of silver, nickel, and iron, containing approximately 40 ml of molten 70-per cent caustic, were successively heated to 75 °C for 10 hours and then allowed to cool to solidification for 2 hours. This heating and cooling cycle was carried on continuously for a period of 6 days. Similar tests were made in which the temperature of the caustic was 110 °C. This temperature, it is believed, corresponds to practice in removing 70-per cent caustic soda from railway tank cars.

The tests were divided into periods of 1-day and 5-day duration of the heating and cooling cycle. The silver crucibles used were commercially available 999.7 fine silver. The nickel crucibles contained 0.005 per cent copper, 0.13 per cent iron, a trace of sulfur, and 99.86 per cent nickel.

The following comparison of the weight losses resulting from heating commercial 70-per cent caustic soda to 75 °C and cooling to solidification indicates that silver corrodes slightly during the first period, and

that there is very little additional corrosion after that time. In the case of the nickel and iron, this conclusion cannot be drawn.

Table 7.—Corrosion Resistance of Silver, Nickel, and Iron to 70-per cent Caustic Soda at 75 °C.

	—Average Weight Loss— (grams) (%)	
Silver:		
(a) 1 day	0.0016	0.0042
(b) 5 days	.0016	.0041
	Increase of (b) = 0.0%	
Nickel:		
(a) 1 day	0.0019	0.0057
(b) 5 days	.0037	.0110
	Increase of (b) = 100%	
Iron:		
(a) 1 day	0.0132	0.0425
(b) 5 days	.0815	.2670
	Increase of (b) = 520%	

There was no apparent color change in the silver-caustic and nickel-caustic solutions. The presence of iron in the caustic was noted upon washing into a sample container, when an excess of water caused the precipitation of a brown substance, apparently ferric hydroxide.

Caustic soda supplied from two commercial sources was used in the tests made of the attack of 70-per cent caustic soda at 110 °C upon silver and nickel. The following are the weight losses observed in the silver and nickel crucibles; the average of tests run in triplicate is reported.

Table 8.—Corrosion Resistance of Silver and Nickel to 70-per cent Caustic Soda at 110 °C.

	(grams) —Caustic A—	—Average Weight Loss— (%)	(grams) —Caustic B—	(%)
Silver:				
(a) 1 day	0.0009	0.0022	0.0019	0.0046
(b) 5 days	.0004	.0010	.0005	.0013
Nickel:				
(a) 1 day	0.0009	0.0025	0.0019	0.0062
(b) 5 days	.0028	.0086	.0031	.0085

Following is a comparison of the corrosion rates of the 1-day and the 1-6 day tests (a and b respectively):

Silver:

Caustic A = (b) is 55% less than (a)  
Caustic B = (b) is 72% less than (a)

Nickel:

Caustic A = (b) is 250% greater than (a)  
Caustic B = (b) is 37% greater than (a)

Several silver-rich alloys containing additions of arsenic, antimony, aluminum, silicon, and manganese were partially immersed in 70-per cent caustic soda at 110 °C for three days. The metal samples were suspended vertically from a glass hook and were not in contact with the silver crucible containing the caustic. The following are the weight losses of these silver-alloy samples in Caustic B.

Table 9.—Corrosion Resistance of Silver Alloys in 70-per cent Caustic Soda at 110 °C for Three Days.

Composition	Weight Loss (grams)	Corroded Area (sq dm)	Weight Loss (mg/sq dm/day)
Ag+ 19.82% Mn	0.0002	0.2270	0.29
Ag+ 16.16% Mn	.0007	.0800	2.92
Ag+ 2.63% Mn	.0001	.0760	0.44
Ag+ _____	.0000	.1300	0.00
Ag+ 7.50% Cu	.0011	.1220	3.06
Ag+ 5.80% Sb	.0013	.1600	2.40
Ag+ 0.23% Si	+ .0002	.1000	+ 0.35
Ag+ 0.78% Si	.0010	.1900	1.75
Ag+ 1.53% Si	.0010	.0900	3.70
Ag+ 2.56% Si	.0024	.1700	4.70
Ag+ 2.50% Al	.0011	.1500	2.45
Ag+ 2.28% As	.0003	.1400	0.72

**Sodium Iodide, Fused.**—Silver is corroded by fused sodium iodide.<sup>7</sup>

**Sodium Nitrate.**—Aqueous solutions of nitrates do not corrode silver, but fused sodium nitrate attacks it with formation of silver nitrate.<sup>6</sup>

**Sodium Polysulfide.**—Silver sulfide is formed by attack of solutions of sodium polysulfide.<sup>6</sup>

**Sodium Peroxide.**—Silver is rapidly attacked by fused sodium peroxide.<sup>49</sup> A gray crystalline substance is formed, a mixture or compound of silver and silver oxide.<sup>18</sup>

**Sodium Persulfate.**—Silver cannot be used in contact with this chemical.<sup>10</sup> The metal gradually goes into solution and a black oxide deposit is formed.<sup>41</sup>

**Sodium Phosphate.**—According to Rogers, Schoonover, and Jordan, steam-jacketed kettles of silver give years of satisfactory service in the preparation of the sodium salts of phosphoric acid.<sup>14</sup> Fused sodium phosphate, however, attacks silver.<sup>10</sup>

**Sodium Sulfate.**—Silver is not attacked by solutions of this salt in the dyestuff industry.<sup>2</sup>

**Sodium Sulfide.**—Solutions attack silver slowly, forming silver sulfide. The fused salt attacks silver rapidly.<sup>7</sup>

**Sodium Thiosulfate.**—Solutions of sodium thiosulfate (hyposulfite) are used as solvents for silver in leaching. In practice the silver is first converted to silver chloride to increase its solubility.

**Steam.**—See **Water Vapor.**

**Stearic Acid.**—See **Fatty Acids.**

**Sulfur.**—Silver is attacked by sulfur at all temperatures. At high temperatures the attack becomes rapid.<sup>6, 10, 18, 53</sup>

**Sulfur Dioxide.**—The gas reacts with silver to form silver sulfide and sulfate. At ordinary temperatures the attack is inconsiderable except for surface tarnishing, but at red heat it becomes strong.<sup>6, 18</sup>

**Sulfur Monochloride.**—Silver, copper, and zinc are only slightly affected, while aluminum, iron, and tin are attacked.<sup>54</sup>

**Sulfur Trioxide.**—Silver is attacked, forming silver sulfate.<sup>6, 46</sup>

**Sulfuric Acid.**—Silver is easily attacked at ordinary temperatures by sulfuric acid of concentrations greater than 60 per cent (sp. gr. 1.71 and over).<sup>2, 6, 10, 16, 18</sup> The attack increases with increasing temperature. Dilute solutions have a very feeble action on silver.<sup>2, 7, 10, 16, 18, 25, 55</sup> Nowack and Spanner<sup>6</sup> and McDonald<sup>56</sup> observed the following weight losses of pure silver: Sulfuric acid of specific gravity 1.355 (45.4-per cent) dissolved 0.794 gram per square meter per hour at 123 °C, and sulfuric acid of specific gravity 1.80 (85-per cent) dissolved silver immediately at 270 °C. Salkowski<sup>55</sup> states that boiling 10-per cent sulfuric acid attacks metallic silver to a very slight extent and that the slight solvent action does not appear to depend upon the presence of oxygen. Sulfur dioxide is not liberated during the process.

Hendrixson<sup>25</sup> observed that about 0.4 mg of finely divided silver dissolved in a very dilute sulfuric acid for every gram of silver taken, but that continued heating did not show any increased solution of silver in the dilute acid. Further experiments by Hendrixson showed that only dilute acid is incapable of dissolving finely divided silver; above a concentration of 74 per cent, attack by the acid began. It is stated that the apparent solvent action is due either to the oxygen of the air, oxygen dissolved in the acid, or to that derived from some external source.

Nowack and Spanner<sup>6</sup> investigated the attack of concentrated and 50-per cent sulfuric acid upon silver and several silver alloys. They found that silver and silver-alloy samples were quickly dissolved in hot concentrated sulfuric acid. In 50-per cent sulfuric acid at 100 °C silver and several silver alloys when completely immersed were observed to have extremely small weight losses; in the most unfavorable example the weight loss was such that a layer 1 mm thick would be dissolved in four years. The solid-solution alloys were superior to the heterogeneous alloys. Nowack and Spanner observed also that the attack of 50-per cent acid at 100 °C was accelerated upon saturating the solution with oxygen. The silver that does dissolve is present in solution as silver sulfate.

The present authors observed the corrosive attack of boiling solutions of 10-, 20-, and 60-per cent sulfuric acid; the tests were conducted as outlined in the general testing procedure.

Table 10 lists the weight losses of samples of silver, Monel, and nickel in boiling sulfuric acid solutions.



Table 10.—Corrosion Resistance of Silver, Monel and Nickel in Sulfuric Acid Solutions at Boiling Temperature (+ = gain in weight).

Material	Length of Test (hrs)	—B (liquid-vapor junction)— (%) (mdd)		(%)	↓ (liquid)— (mdd)
10-per cent H <sub>2</sub> SO <sub>4</sub>					
Silver	0-24	0.08	2.00	0.09	2.40
	24-96	.03	.25	.08	.70
No change in solution.					
Monel	0-18	0.37	123.00	0.20	70.00
Solution turned yellow.					
20-per cent H <sub>2</sub> SO <sub>4</sub>					
Silver	0-24	0.00	0.0	0.16	4.00
	24-96	+ 0.37	+ 3.2	.50	4.50
	90-216	+ 0.45	+ 2.3	.10	1.00
No change in solution.					
Nickel	0-24	2.90	830.0	3.20	868.00
	24-96	6.10	570.0	6.20	503.00
Solution became green in color.					
Monel	0-24	0.10	33.5	0.10	24.00
	24-96	1.30	120.0	1.70	156.00
	96-216	6.00	336.0	7.20	390.00
Solution became green in color.					
60-per cent H <sub>2</sub> SO <sub>4</sub>					
Silver	0-24	0.60	14.40	1.00	26.0
	24-96	Samples cut into two parts at junction.		30.00	252.0
No color change in solution.					
Monel	0-24	6.50	1837.0	4.90	1355.0
	24-96	Specimens cut into two parts at junction.		20.20	1790.0
Solution assumed a green color.					

**Sulfuryl Chloride.**—Although gold and platinum are attacked by sulfuryl chloride (SOCl<sub>2</sub>) after prolonged heating at 150 °C, and iron is also attacked, silver, zinc, and cadmium do not react even at 300 °C.<sup>57</sup> A protective silver chloride coating is formed.<sup>6</sup>

**Tanning Solutions.**—Silver or silver-lined vacuum pans have been used in tanneries.<sup>58</sup>

**Tartaric Acid.**—There is no attack on silver.<sup>7</sup>

**Tetraethyl Lead.**—Silver is corrosion-resistant to tetraethyl lead and leaded gasoline.<sup>15</sup>

**p-Toluyaldehyde.**—Silver is attacked at 50 °C.<sup>6, 10</sup>

**Urea.**—In a study of the system urea-water-ammonium carbamate, Thompson, Krase, and Clark<sup>59</sup> tested 36 corrosion-resistant metals and alloys for their resistance to the solutions at 142 °C under pressure. Silver ranked second in corrosion resistance, exceeded only by Duriron. The losses by the first five, in mg per sq cm per day, were: Duriron 0.012, silver 0.026, illium G 0.066, chromium 0.084, and lead 0.11. These figures were obtained in a 7-day test. A 4-day test showed differences

in the case of some metals, but did not affect the relative position of silver.

Silver liners are being used in apparatus for synthesis of urea from ammonia and carbon dioxide.<sup>15</sup>

**Vinegar.**—See **Acetic Acid**. Absence of color is of great importance in making white vinegar, and silver has been used for this reason.

**Viscose.**—Silver equipment is usually not employed because of the sulfurous nature of the substances.<sup>2</sup> See also **Artificial Silk**.

**Water.**—From the standpoint of corrosion, silver is wholly insoluble in pure water<sup>6, 14, 18</sup> at all temperatures. A very small amount of solution will, however, take place in the form of silver ions, and this accounts for the bactericidal action of silver, which is found to decrease proportionately as the silver is removed.<sup>60</sup> The amount of solution was determined by Kepelka and Toul at Prague.<sup>61</sup> They kept pure leaf silver in contact with pure distilled water in a glass vessel at room temperature in darkness, and found the following amounts dissolved per liter of water:

Period	Grams of Silver in Solution
7 days	0.000012
14 days	.000021
21 days	.000035
180 days	.000036

The saturation point (equilibrium) is reached just after 21 days.

**Water Vapor.**—Silver is not appreciably attacked at any temperature.<sup>6, 10</sup>

**Wines.**—Bottle caps or crowns containing a spot of pure silver foil can be used to advantage in sealing of high-pressure wines. Those used thus far are considered too expensive for ordinary bottling purposes, but bottles with this type of crown are used for checking in taste tests.<sup>62</sup>

**Zinc Chloride.**—Silver is not attacked by zinc chloride solutions in the dye-stuff industry.<sup>2</sup>

**Zinc Oxide.**—There is little or no attack by this compound on silver.<sup>18</sup>

#### RESISTANCE OF SILVER ALLOYS TO CORROSION BY A SODIUM CHLORIDE SOLUTION

Corrosion tests sponsored by the Silver Research Project were conducted at Columbia University by Colin G. Fink and V. S. de Marchi.<sup>63</sup> The investigation was prompted by the possibility that the good resistance of silver to chloride corrosion might be imparted to other metals by addition of silver. The main purposes of the tests were (a) to determine the effect of adding silver to certain metals and alloys on their resistance to corrosion by a 3-per cent brine solution under stated conditions; and (b) to obtain comparative figures on the resistance of certain silver-rich alloys to corrosion by this solution. Some tests on anodic corrosion were also made. The results are summarized in the following pages.

All the tests with the 3-per cent solution of sodium chloride were made with a machine which alternately immersed the specimens in the solution for 15-minute periods and then exposed them to the atmosphere for 15-minute periods. The total length of the test was either one, two, or three weeks. Before the test the samples were cleaned with steel wool, washed in alcohol, rubbed with a clean towel, rinsed in carbon tetrachloride, and weighed. When they were removed from the corrosion machine they were washed with water, rubbed with a bristle brush, washed in alcohol, rubbed with a clean towel, rinsed in carbon tetrachloride, and weighed.

### Silver-poor Alloys

The tests indicated that additions of silver in various amounts were beneficial to corrosion resistance in a small number of instances. These were as follows:

**Zinc.**—Although the addition of silver to zinc in amounts of 1 to 21 per cent resulted in lowered corrosion resistance, the alloy containing 31.4 per cent silver was found to be fairly resistant to the solution, considerably more so than pure zinc.

**Copper-zinc.**—The rather low chloride corrosion resistance of the 60:40 Cu-Zn alloy (Muntz metal) appeared to be benefited by the addition of either 0.1 or 1.0 per cent of silver. A chloride film was formed on the samples, causing gain instead of loss in weight.

**Copper-aluminum.**—Improvement was noted by addition of silver to the 90:10 Cu-Al alloy in some cases, especially with 1.15 per cent of silver. The results, however, were not consistent.

**Aluminum-magnesium.**—Addition of 1 per cent of silver improved the corrosion resistance of the 90:10 and 80:20 Al-Mg alloys. Silver in the amount of 0.1 per cent had no effect, while 5 per cent of silver had an adverse effect.

**Magnesium-tin-manganese.**—A slight improvement was found by adding 1.5 per cent of silver to the 93.5:6:0.5 Mg-Sn-Mn alloy. The corrosion resistance was still inferior, however.

Little or no effect was found from additions of silver in various amounts to the following alloys:

Copper-zinc: 90:10 Cu-Zn.

Copper-aluminum: 95:5 Cu-Al.

Copper-tin: 95:5, 90:10, and 80:20 Cu-Sn.

Copper-silicon-manganese: 96:3:1 Cu-Si-Mn.

Aluminum-magnesium: 96:4, 90:10, and 80:20 Al-Mg with 0.1 per cent silver.

A detrimental effect on corrosion resistance was found from addition of silver in various amounts to the following metals and alloys:

Aluminum

Lead

**Zinc**

Armco iron (0.002 per cent silver)

Copper-zinc (the 80:20 and 70:30 Cu-Zn alloys)

Copper-beryllium (Be 1 to 2.25 per cent)

Aluminum-zinc (5.5 to 33 per cent zinc)

Aluminum-magnesium (the 96:4, 90:10, and 80:20 Al-Mg alloys with 5 per cent silver)

Aluminum-silicon (Si 2, 4.5, and 12.5 per cent)

Magnesium-zinc (7 to 20 per cent zinc)

Magnesium-tin (6 to 7 per cent tin)

**Silver-rich Alloys**

**Silver-aluminum.**—Aluminum added to silver in the amounts of 2.5 to 12.5 per cent progressively decreased the corrosion resistance in 3-per cent brine solution.

**Silver-aluminum-titanium.**—Certain silver-aluminum alloys to which 0.12 to 0.14 per cent titanium was added were tested. Good corrosion resistance was reported for the one containing 5.93 per cent aluminum, but one containing 6.14 per cent aluminum had a rather high corrosion loss. In alloys of 7.9 and 16.3 per cent aluminum, rapid corrosion continued after the samples were removed from the test and dried.

**Silver-silicon.**—Silicon up to 6 per cent generally decreased the corrosion resistance. However, some inconsistent results with gains of weight were obtained.

**Silver-copper-silicon.**—Cu-Si additions to silver were detrimental.

**Silver-manganese.**—0.75 per cent of manganese was detrimental. Large gains of weight were recorded with the samples containing 4 and 10 per cent of manganese.

**Anodic Corrosion in Saturated Brine Solution**

Silver and silver alloys were used as anodes in an electrolyte of saturated sodium chloride solution with cathodes of graphite. The current density at the anode was 20 amperes per square foot. The runs lasted 3, 4, or 6 hours. With silver and alloys containing a very high percentage of silver a brownish film, probably of silver oxide, formed on the surface of the anodes. The film had very poor adhesion qualities. All the other alloys tested decomposed when undergoing this anodic corrosion test.

The results obtained in these tests were not at all comparable with the exceptionally low anodic corrosion results obtained by Fink and Pan in their extensive work looking toward the development of insoluble anodes for the electrolysis of brine.<sup>157, 158</sup> Using a 5 per cent brine solution, they found that a small amount of silver added to lead, or a small amount of lead added to silver, reduces the solubility to less than 1 per cent of the solubility of the pure metal. Besides Ag-Pb alloys, they

investigated some Hg-Pb, Ag-Pb-Hg, and Ag-Pb-Mn alloys. The Ag-Pb series gave the best results and an anode composed of 61 per cent silver, 39 per cent lead was practically insoluble. The very low corrosion rates were due to the formation of a film, chiefly of lead oxide and silver chloride, which protected the anode and was itself insoluble in the 5 per cent brine. The rate of corrosion was found to increase rapidly with concentration of the brine as well as with temperature. It is believed that the protective action of the film was in part due to catalysis of chlorine gas liberation.

#### TARNISHING OF SILVER AND SILVER ALLOYS

The use of silver for ornamental or decorative purposes is subject to the detriment of the formation of a dark coating on the metal under ordinary atmospheric conditions. The general appearance of the film, the comparatively short time required for it to form, and the labor involved in its removal are matters of common knowledge. The film is composed chiefly of silver sulfide. Many investigations have been made of its formation and of methods of combatting it; the more important practical aspects of the information which these have yielded will be summarized here.

The color of the film varies, passing through the range of light interference colors with increasing thickness, soon becoming a dark greenish-brown to black, the latter being the true color of silver sulfide. The protective action of the film is such as to retard its progressive formation, and it rarely if ever becomes important from the standpoint of loss of silver. Although it is a form of corrosion, its results are not of the serious character usually implied in that term; accordingly it is usually called "tarnishing."

The electrical conductivity of silver sulfide is high for a compound. While its resistivity is about 10,000 times that of copper,<sup>159</sup> a thin tarnish film of it will offer but little electrical resistance. Obviously, however, electrical contacts will be most efficient if kept clean.

The most important cause of tarnishing is the presence of minute amounts of hydrogen sulfide ( $H_2S$ ) in the atmosphere. Other sulfur compounds, however, will produce the same effect, and sulfur dioxide ( $SO_2$ ) has been shown to be an important contributing cause. While silver sulfide ( $Ag_2S$ ) is always the predominating constituent of the film, and some authorities have stated that it is the only constituent, Price and Thomas<sup>64, 65</sup> found that when sulfur dioxide and water vapor were present in greater concentration, as over gas stoves, the film was a mixture of the sulfide and the sulfate ( $Ag_2SO_4$ ). Certain foods, such as egg yolk and onions, and certain substances, such as vulcanized rubber, produce rapid tarnishing due to their sulfur contents.

Under usual conditions sterling silver tarnishes more rapidly than pure silver. Vinal and Schramm<sup>66</sup> found that the rate of tarnishing of

silver-copper alloys was in most cases proportional to the copper content. The tarnish on sterling contains copper as well as silver compounds, the relative amounts varying with conditions. Tarnishing rates on silver and silver alloys are accelerated by increased moisture in the air as well as by increased concentration of sulfur compounds.

### Removal of Tarnish

The action of silver detarnishing agents may consist of chemical attack, abrasion, or a combination of the two. Most household silver "polishes" depend chiefly on fine abrasive constituents which require rubbing in use. Dilute solutions of sodium or potassium cyanide dissolve most silver compounds readily and are often used in industrial cleaning; they are objectionable in household cleaners because of being violent poisons. Another objection is that they attack the silver itself as well as the film. Tarnish on pure silver can be removed by simple heating below a red heat, since the sulfide film decomposes in air at about 400 °C. Heating sterling silver, on the other hand, increases tarnishing because of oxidation of copper, while heating of silver-plated ware should also be avoided.

The best household method of cleaning tarnished silver and silver alloys is the "electrolysis" method. The materials are readily available at slight cost and labor is minimized. No electricity is needed for the process; the effect depends on the slight galvanic action which is automatically produced. This results in production of hydrogen ions which react with silver sulfide, reducing the film to silver with formation of hydrogen sulfide. Thus no loss of silver is involved unless the piece is subsequently rubbed.

The electrolytic method has been studied by Vinal and Schramm.<sup>66</sup> They state that if the tarnish film is thin, the cleaned silver retains a satisfactory luster, but if too thick the reduced "mossy" silver will give the surface a dull appearance, and some polishing will be desirable to restore brightness. With ordinary films they found that abrasive cleaners resulted in 30 to 70 times as great a loss of silver as the electrolytic method; but even with abrasion the loss is so small as to be negligible on solid silver, though not on thin-plated material.

The process consists of immersing the silver to be cleaned in a hot solution of sodium carbonate or bicarbonate ( $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ ) and chloride ( $\text{NaCl}$ ), having the silver in contact with a base metal. For the latter, aluminum is most often used; magnesium, zinc, and tin are also satisfactory. The strength of the solution may vary widely without great difference in effect; a teaspoonful of the salt to a quart of water is often recommended, which corresponds roughly to 0.1*N*. Vinal and Schramm tested 0.1*N* solutions of  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , equal parts of  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$ , and equal parts of  $\text{NaCl}$  and  $\text{NaHCO}_3$ . The base metal is anodic to the silver; it will become coated with an anode film which needs to be removed occasionally by abrasion to per-

mit good metallic contact with the silver. If this is not done when plated silverware is being cleaned, any exposed portion of the basis metal will act as anode and become corroded. Though no special size or shape is necessary, several commercial devices may be purchased. Some of these are constructed of two metals, such as zinc and tin, in which arrangement tin is anodic to the silver and is said to be kept free from film because it is cathodic to the zinc.

### Prevention of Tarnish

Attempts to prevent tarnishing have been made both by means of coatings and by means of alloying. Jordan, Grenell, and Herschman<sup>67, 68</sup> prepared a large number of silver alloys containing from 1 to 25 per cent of the alloying metals, including binary, ternary, and a few quaternary alloys, determined their principal physical properties, and compared their tarnish-resistance qualities by short exposure to moist air containing relatively high concentrations of hydrogen sulfide (1 and 2 per cent) and sulfur dioxide (5 per cent), as well as by dipping in 0.1*N* sodium sulfide solution containing excess sulfur. They found that alloys of silver with cadmium or zinc were the most tarnish-resistant of the binary alloys, and that the addition of antimony or tin or both to a silver-zinc base in amounts such that the sum of all the alloying metals did not exceed 7.5 per cent (to give sterling fineness or better), produced workable alloys of marked tarnish resistance and of greater strength than any of the tarnish-resistant binary alloys. They did not find any alloy, however, that could be described as "non-tarnishing" and concluded that the development of such an alloy (silver-rich) is unlikely. They point out also that manufacturers do not favor an alloy which is only "tarnish-resistant" and not completely "non-tarnishing," nor is an alloy of less than sterling fineness in silver likely to be acceptable. The regard of the public for sterling, as well as its working properties and manufacturing details, all point to the conclusion that for an alloy to have wide commercial application it would have to possess much greater tarnish-resisting properties than any yet developed. Also, most of the alloys are inferior to fine silver and sterling silver in color.

Vernon<sup>69</sup> compared the loss of reflectivity by fine silver, sterling silver, and a special cadmium-containing sterling (1.75 per cent Cd) after 16 days' exposure in kitchen atmospheres. With polished samples fine silver lost 71 per cent of its original brightness, while sterling lost only 16.5 per cent and the special sterling 8.3 per cent. With dull-surface samples, however, each lost about the same.

Tarnish protection by coating has the disadvantage of alteration in the surface and therefore usually affects the appearance of the silver. Furthermore, if the object is to be handled or subjected to wear or possible scratching, the silver will tarnish where exposed. Plating silver with rhodium has met with approval in some cases, the difference in appearance being small, but this is merely begging the question. Nearly

invisible lacquers have been used, but they are easily scratched or removed. Lacquers containing amber recently developed in Germany are said to offer some promise.<sup>70</sup> Alloying with indium by thermal diffusion of an electrodeposited surface has been tried, but the color is not satisfactory.<sup>160</sup>

The best application of the coating method to date appears to be given in the recent extensive work of Price and Thomas,<sup>64, 65</sup> embracing the testing of over 70,000 samples, which included over 100 different silver alloys. Exposure for periods up to one year were made in a wide variety of locations, chiefly kitchens and living rooms. These investigators employed a film of oxide of aluminum, beryllium, or silicon on silver, made possible by making an alloy of the silver with a small percentage of the other metal and then heating it in hydrogen containing 0.1 mm partial pressure of water vapor. Heating in air cannot be employed, since this causes the film to contain silver oxide as well as the oxide of the other metal, and the mixed oxide film is not sufficiently tarnish-resistant. This method is effective even with as little as 1 per cent of aluminum or beryllium in the silver. No silver alloy was found which would form a satisfactory film autogenously. Another method of producing the single oxide film on silver or a silver alloy was by electrolysis, using the silver as cathode in a solution of aluminum or beryllium salts.

Table 11.—Relative Tarnish Resistance of Silver.

Conditions of Tarnish Test	Predominant tarnish color of specimens after test <sup>1</sup>				
	Black	Purple	Brown	Yellow	Negligible
A 45 minutes; 2% H <sub>2</sub> S, 5% SO <sub>2</sub> Moist air	15; 10 Mg 7.5 Cu 2; 4 Te	5; 2 Mg Specimen A 10; 15; 5 Al 2; 4 Mn 2 Ni Pure silver 5; 10 Si 1 Bi 15 Sn 5 Cd	0.14; 0.77 Cr 5 Sb 10; 5 Sn 10; 15 Cd 5; 10; 15 Zn 4.5 Cd, 0.5 Ni 4.7 Zn, 0.6 Ni	20; 25Cd Specimen B 1.6 Sb, 0.6 Ni, 0.1 Cr 3.5; 5; 7.5 Zn 4.7 Zn, 0.2 Cr 5.6 Sn, 0.8 Ni 4.7 Cd, 0.06 Cr 5.2 Sn, 1 Cr 3.5 Sb, 1 Ni 5.3 Sb, 1.2 Cr 4.6 Zn, 2.7 Sb 5.2 Zn, 1.9 Mg 5.2 Zn, 2 Sn	15 Sb 20; 25 Zn 4.4 Zn, 2.1 Sb, 1 Sn 4.5 Zn, 2.1 Sb, 0.7 Al 4.6 Zn, 2.7 Sb 4.5 Zn, 2.3 Al
B 24 days Crystals: Boric Acid and K <sub>2</sub> S: Moist Air	7.5 Cu	10.0 Cu, 0.99 Si 4.96 Cu, 0.47 Si	7.47 Cu, 0.54 Si 2.51 Cu, 0.20 Si 3.37 Cu, 3.78 Si 0.78 Si	5.93, 0.13 Ti Pure silver 5.1, 2.5 Al 0.75 Mn 0.25; 1.53; 2.56 Si	1.47 Si 0.23 Si, 0.06 Ni 17.92; 4.06 Mn 3.89; 6.09 Si
B 47 hours Crystals of K <sub>2</sub> S in atmosphere pro- duced by saturated solution of K <sub>2</sub> H <sub>2</sub> O <sub>3</sub>		7.5 Cu	Pure silver 11.84; 6.76 Sb 5.80 Sb 2.28 As 16.16 Mn	6.62; 19.82 Mn 2.63 Mn 23.66; 20.35 Sb	46.24 Sb

<sup>1</sup> Within each block of the table the alloys are arranged in the approximate order of increasing resistance to tarnish.

Specimen A—92.9 Ag, 0.4 Ni, 2.6 Cu, 3.9 Zn } Commercial tarnish-resisting silver alloys.

Specimen B—92.8 Ag, 3.4 Cd, 3.2 Sb

A Tarnish-resisting Silver Alloys, Technologic Paper No. 348 of National Bureau of Standards.

B Experimental results, American Silver Producers' Research Project.

These films are transparent and are highly protective against tarnishing. Though Price and Thomas found their films invisible when the formation was properly regulated, Powell stated that all those produced by him caused a "bloom" on the surface and were therefore not invis-



ible. Close control is necessary in both heating and electrolytic methods, and there is doubt as to whether the process will prove industrially practicable. Further development work, however, is in progress. Tests of durability and wear resistance have been promising. The method may prove to be advantageous in combatting corrosion of silver (and other metals also) by some chemicals as well as in combatting tarnish.

Immersion of silver in certain chemicals has also been found effective in preventing or retarding tarnishing. Assman<sup>71</sup> states that an invisible film of silver chromate, formed by immersion for 3 to 6 minutes in 10 per cent solution of potassium dichromate, gives good protection without change in appearance of the silver. Finckle<sup>72</sup> has patented a process of immersion in chromic acid.

As a matter of routine the Bureau of Standards fellowship has made comparative determinations of the tarnish resistance of all the silver-rich alloys prepared. While no striking results were achieved the data are given in Table 11 as a matter of record. In each group of tests there will be found a sample of pure silver and a sample of sterling; these will serve as standards against which to compare the behavior of the other samples tested.

## Chapter 16

### The Oligodynamic Effect of Silver

By A. GOETZ,\* R. L. TRACY † and F. S. HARRIS, JR.‡

#### I. THE FUNDAMENTAL PHENOMENON AND ITS HISTORY

The experience that a large number of metals, particularly the heavy metals, have germicidal properties when they are brought into contact with germ-containing liquids, reaches very far back into the ancient Mediterranean as well as the Asiatic cultures. Surgical prescriptions mention, for instance, the use of silver foil or plates for insertion into wounds or replacement of missing bone fragments; the use of silver and gold as material for containers of beverages to prevent spoilage or transfer of infectious diseases, the destructive effects on marine growth on ships' bottoms by copper plates, are a few examples which demonstrate how widely the destructive effects on primitive life of minute traces of the heavy metals must have been known.

The first systematic scientific investigations in this field are due to the great Swiss botanist Carl Nägeli (1893)<sup>1</sup>, who described the phenomenon in most of its aspects which, even in the light of present knowledge, must be considered fundamental. Thus a brief summary of his findings appears to be justified:

(a) When pure water was brought into contact with clean metallic surfaces (copper coins) it was found to be lethal to spirogyra in less than one minute, although the mass concentration of the metal in the water was only of the order of  $10^{-8}$  or even as low as to  $10^{-9}$ , as proved by subsequent analysis of very large quantities of this water.

(b) If the metal was removed and the glass container drained of its contents and refilled with fresh water, it soon acquired the same lethal qualities *although it had not been in contact with the metal*. Subsequent drainings and refilling with fresh water showed that the effect faded only very gradually. Nägeli traced the cause of the "activation" of the water to the glass walls of the container, which had originally adsorbed comparatively large quantities of the metal which later had gone in solution, *i.e.*, the walls "reevaporated" this metal back into the fresh water, rendering it active. The consequences of this adsorptive process can thus be opposite: if the liquid contains only low metal concentrations, the walls

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will adsorb the metal almost completely, rendering the water *inactive*; or, whenever the metal "storage" on the walls from previous contact is sufficiently large, they can *activate* fresh water. Aside from the walls of the vessel it was found that any neutral colloidal surface, such as cotton, starch, gums and glue, renders the liquid inactive in a very short time, whereas substances which dissolve in molecular dispersion, such as the sugars, have no apparent effect upon the activity of the water. The former serves as an explanation of the fact that water found in lakes, ponds and rivers, in spite of the undeniable presence of metals or metallic compounds, is in general not active.

(c) The lethal effect upon a given organism depends largely upon the cell population, for small populations are killed very fast, larger ones at slower rates, and the very large are not affected at all. The effect is also largely dependent upon the type, age, etc., of cells.

In view of the lethal effect of metal concentrations, which are beyond the capacity of chemical analysis, Nägeli called the phenomenon the *oligodynamic effect* (from the Greek oligos = few, and dynamis = power). This concept, although only phenomenologically defined, has entered into a voluminous literature which has described and studied the problem from the physicochemical, colloidal, biochemical and physiological point of view. Before going into details of this somewhat involved subject, the points mentioned above should be enlarged in some respects.

Although Nägeli performed his experiments chiefly with copper, it has since been found that most metals can be oligodynamically active, although authors differ widely about the degree of activity. The metals which have been studied are the following, in their approximate order of activity: Cu, Ag, Hg, Cd, Zn, Mg, Pb, Sn, Pd. Very little effect is attributed to Al, Cr, Fe, Bi, Au and Pt.<sup>2, 3</sup> For reasons given below, not much importance can be attached to such lists of metals, as the mechanism which puts the metal into solution varies with the chemical nature of the metal and with the experimental technique used. Whenever a metal oxidizes easily and has soluble oxidation products, the rate at which metal ions enter into solution is necessarily larger than in the opposite case; and as the effective concentrations are in general beyond the limits of a quantitative measurement\* it is very difficult to decide

\* To measure the small amounts of Ag characteristic of oligodynamic activities the following methods\* have been used:

(a) A colorimetric test with *p*-dimethylaminobenzalrhodanine, with a sensitivity of 1 part in  $5 \times 10^5$  (Fiegl, Kolthoff) a modification of this test employing adsorption on a collodion membrane is sensitive to 1 part in  $4 \times 10^7$  (Ettisch and Tamchyna). The procedure developed by the Bureau of Standards gives a direct test in the range 60 to  $9 \times 10^3$   $\gamma$ /liter [Schoonover, (A)].

(b) A colorimetric test with pure methylene blue reduced to the leuco-compound of Na formaldehyde-sulfoxylate (Schumacher).

(c) Potentiometric methods which are sensitive to about 1 part in  $10^8$  (Krause, Krepelka and Toul, Hosenfeld).

(d) After concentrating in the water by suitable means, the Ag is removed electrolytically from an alkaline bath and finally determined volumetrically with .001N iodide solution, using rhodanine as an indicator (Egg).

whether the high activity found is due to a higher concentration of metal ions or to a higher specific activity of the metal.

It may also be mentioned at this point that it appears necessary to restrict the application of the term oligodynamic activity to certain processes in which extremely low concentrations of metal ions are involved, in contradistinction to the well-known lethal action of the salts of heavy metals, such as sublimate, copper sulfate, arsenic, etc., at high concentrations, although the physiological effect of such metal poisons may be in many cases identical with the consequences of the oligodynamic phenomenon. On the other hand, one should *not* restrict the term only to those processes in which the metal goes directly into aqueous solution without obviously present anions, as experiments have borne out that the type of process used for dissolving the metal does not affect the germicidal effect, and that at oligodynamic concentrations the anion is of no germicidal consequence (see later).

In view of practical applications it appears that silver is best suited as an oligodynamic material because of the extremely slight solubility of most of its salts, which fact renders it almost impossible for large concentrations of silver ions to occur in higher organisms. This particular property singles silver out from the host of other oligodynamic metals which may have the same activity, and renders it practically harmless to animals and humans. Consequently in this chapter the interest will be focused chiefly on the use of this metal, particularly as there is little doubt that the results obtained with silver can be applied to the other metals without major alterations, as far as the oligodynamic ranges of concentration are concerned.

A typical property of oligodynamic water is the lack of permanency, of its activity in absence of the metal source, since the walls of the container, as well as any colloid in the water, have a tendency to adsorb the metal and thus decrease the activity of the water. It is, of course, possible to produce an equilibrium between the metal concentration on the walls and in the liquid, which is reached when the walls "re-evaporate" as many ions into the liquid as metal ions are "condensed" out of the liquid on the walls. The existence of such an equilibrium requires, of course, not only extended time intervals but also a constancy of temperature so that, unless special precautions are taken, one cannot expect experiments to be reproducible. This may explain a great number of discrepancies in the literature, particularly with regard to quantitative data on germicidal concentrations. It is also very difficult to analyze the concentration quantitatively without disturbing this equilibrium condition.

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(e) A nephelometric method (Krepelka and Toul).

(f) Haber's method of adsorption of the Ag on PbS and determining the amount by fire assay (Freundlich and Söllner).

For references to other methods see Schoonover.

It may be noted that the methods of (c) measure the Ag ion concentration, and that the other methods determine the total Ag present.

If the liquid contains organic colloids, as is the case in most nutrient cultures, the problem is aggravated still more, since an equilibrium not only between the metal-containing liquid and the wall, but also between the former and the colloid, has to be reached before the conditions for a

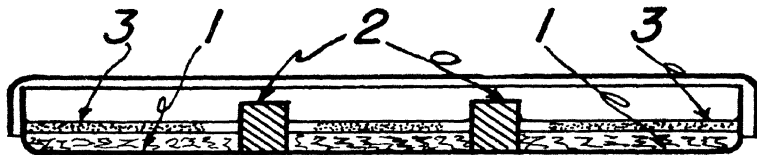


FIGURE 1. Vertical cut through Petri dish arranged for demonstration of oligodynamic activity: (1) non-nutrient hard agar layer; (2) active sample; (3) inoculated nutrient agar layer.

stable and permanent oligodynamic activity are fulfilled. Hence, the effect varies even for the same organism with the concentration and the type of nutrient, and is quite different for liquid media and semi-solid substances such as agar plates.

The "classical" way for demonstrating the oligodynamic phenomenon, first apparently used by Thiele and Wolf,<sup>5</sup> is to place the active material (metal or metal-containing substance) on an agar plate which is subsequently heavily inoculated with bacteria. After the proper incubation time, the opacity of the plate will indicate regions of bacterial growth,

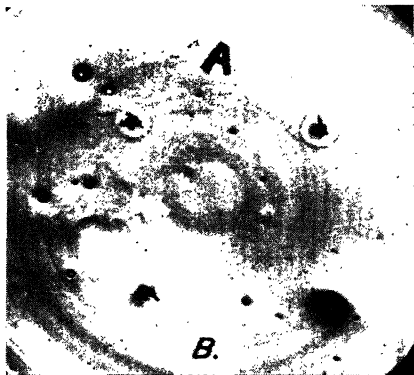


FIGURE 2.

Oligodynamic activity of cleaned silver crystals: "A" washed in cold water (active), "B" washed in boiling water (inactive).

whereas transparent domains (halos) will characterize regions in which no growth occurred due to the oligodynamic activity.

The method used (A)\* in the preparation of agar plates for the

\* As most of the investigations of the authors in the field of oligodynamics have not yet been published elsewhere, the mark (A) is used in the text whenever it refers to the work of the authors of this chapter.

demonstration of the oligodynamic effect (Figure 1) is the following: A Petri dish is first filled, 6-7 mm deep, with a heated, fairly concentrated agar solution (1) into which the samples (2) are imbedded and where they are held rigidly when the agar has hardened. Then a nutrient agar solution (3) containing approximately  $10^9$  cells/cc of *E. coli* is poured over the hardened base to a depth of not more than 2-3 mm. For such large initial bacterial concentrations a uniform opacity will occur after incubation which, however, is restricted to the upper thin layer (2). Hence the "halos" are easily measured because of the nearly two-dimensional shape of the culture.

Figure 2 shows a photographic top view of such an agar plate at approximately half scale. In the agar plate are inserted a number of silver crystals, of which the ones marked as *A* are oligodynamically active, those marked *B* are inactive.

## II. THE PHYSICO-CHEMICAL NATURE OF THE OLIGODYNAMIC EFFECT

Before going into a discussion of the effects to which the metal atoms or ions give rise when in contact with a cell, it appears important to discuss some of the physical and chemical processes which cause the metal first to go into solution.

To many authors this particular phase in oligodynamic activity appears to have been of somewhat mysterious character, as offhand it is not obvious why a metal should go into aqueous solution in the absence of acids or salts which produce a chemical attack on the surface. The obscurity of this primary phenomenon has even led some authors to the assumption that the oligodynamic activity of a metal was due to a force acting over distances similar to radiation or radioactivity.<sup>6</sup>

Most important of all, one fundamental observation must be realized, that if the metal surface exposed to the liquid is *really* clean and without potential, no activity whatsoever can be observed<sup>7</sup> (*A*). If one chooses single crystals of silver which expose their natural surfaces (110) and cleans them chemically, ultimately by repeated boiling in distilled water, the experiment on the agar plate is always negative (Figure 2). The crystals marked *A* were cleaned chemically ( $\text{HNO}_3$ ) and washed thoroughly in distilled water to remove all traces of nitrates; *B* was boiled in distilled water after this treatment and lost all activity. Similarly one can inactivate active silver crystals by heating them in  $\text{N}_2$  or by producing electrolytically a surface layer of  $\text{H}_2$ .

On the other hand, inactive crystals can be rendered active by heating in air or in an  $\text{O}_2$ -atmosphere. The obvious effect of this treatment is the formation of oxide layers at the surface. The same effect can be produced by brief submersion of the crystals in dilute solutions of  $\text{H}_2\text{O}_2$ . Cl, Br and I act in a similar manner by the formation of halide layers. It is not necessary that these layers be traceable in any way, as extremely small quantities suffice.

Quantitative removal of them by boiling water or, *e.g.*,  $\text{Na}_2\text{S}_2\text{O}_3$  destroys the activity completely. Figure 3 shows crystals treated with dilute  $\text{HCl}$  after washing in cold, *C*, and in boiling *H* water. In the latter case only traces of activity are visible on one crystal. A large variety of methods of activation and inactivation based on these principles has been reported.<sup>8</sup>

The reason for the use of (electrolytically) grown crystals is the absence of lattice disturbances which can cause local variations of potential (local element). Experiments (A) have shown that plastically deformed metal, such as drawn wires or fine powders which expose a large area of surface, are not necessarily inactivated with the above methods. The reason for this can be seen in the existence of local potentials at the surface caused by variations of the degree of plastic deformation which results in local electrolytic activities.

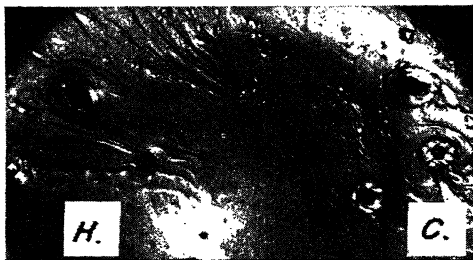


FIGURE 3.

Oligodynamic activity of silver crystal activated in dilute  $\text{HCl}$ : "*C*", after washing in cold; "*H*", after washing in boiling water.

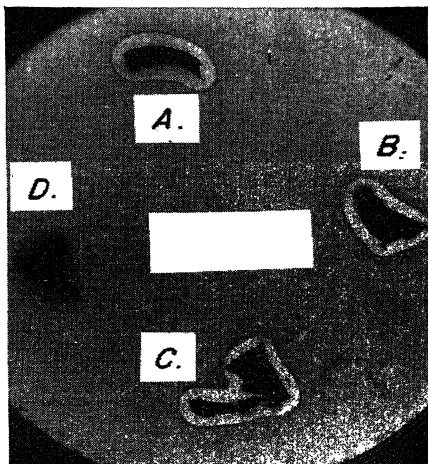
Figure 4 shows the behavior of lumps of extremely fine dispersed  $\text{Ag}$  produced by reduction of  $\text{AgNO}_3$  at high temperature: *A* is the material without further treatment; *B* after being heated to red heat and cooled in air; *C* same as *A* after being boiled in distilled water (activity has not disappeared); *D* same as *A*, but heated and cooled in  $\text{N}_2$  (activity has disappeared completely).

The activation of crystal surfaces is the simplest case of the production of an oligodynamic source where the compound formed at the surface has a certain solubility (see Table 1), thus producing  $\text{Ag}$  ions ( $\text{Ag}^+$ ) in the surrounding medium by its dissociation.

In the case of the occurrence of local potentials the activation does not need to be produced by additional agents, since the potentials will cause local electrochemical polarization. A simple method to demonstrate the production of oligodynamic activity by polarization consists in inserting two silver electrodes in the agar plate (Figure 1) and maintaining between them a potential close to the dissociation potential of the electrolyte without thereby producing a current more than the  $10^{-6}$  amp necessary to compensate for the ion diffusion. As Figure 5 demonstrates, only the anode is active, due to the polarization with oxygen, whereas the cathode

FIGURE 4.

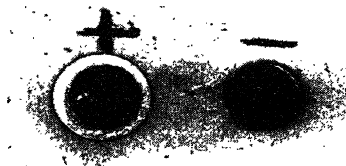
Oligodynamic activity of "amorphous" silver (reduced from  $\text{AgNO}_3$ ): "A", without further treatment; "B", after heat treatment in air; "C", like "A" but cleaned in boiling water; "D" like "B" but treated in nitrogen. The activity of the first 3 samples has not been affected, the last is completely inactive.



loaded with  $\text{H}_2$  is inactive. This effect is quite different from the common electrolytic process as no ions are transported due to the virtual absence of a current, and it proves that the polarization of the electrodes is sufficient for the production of an activity. The anode remains active after its initial formation even if its potential is not maintained; it can be inactivated by depolarization (reversal of potential), by boiling in water, etc. The longer the polarized state is maintained or the more frequently it has been established, the more difficult it is to remove the activity, obviously due to a deeper penetration of the surface reaction into the metal (A).

FIGURE 5.

Oligodynamic activity produced by electrolytic polarization at the silver anode; the silver cathode remains inactive. (Current about  $10^{-6}$  amp).



A very excellent demonstration of the processes which take place in temporary or permanent activation has been given by Fromherz and Heiss,<sup>9</sup> who showed that oligodynamic activity could be produced over the whole surface of an, as such, *inactive* long silver wire by coating one end of it with  $\text{AgCl}$ , thus creating the galvanic element  $\text{Ag-AgCl}$  and



sending silver ions from the *whole length* of the silver wire into the agar. A trivial but impressive extension of the experiment shows that one can produce this activity from an inactive part of the wire in a second Petri dish if the active end of the wire remains in the first dish, while the inactive end is led into the second, provided that in addition a neutral contact between the electrolytes (agar) by means of a curved agar bridge is supplied.

It can thus be taken for granted that the oligodynamic affect occurs only if an active deposit is produced on the metal surface. The activating substance can be chemically or electrochemically deposited if the resulting metal compound dissociates and is soluble. As very small concentrations of ions suffice for germicidal purposes, the solubilities of most silver compounds are sufficient, perhaps the only exception being  $\text{Ag}_2\text{S}$  (see Table 1). A convenient way of producing such active layers is electrolytic polarization; an equally simple but faster process is the use of an

Table 1.—Solubility of Silver Compounds in Water.

Ag Compound		Solubility		Solubility Product
		g/liter	Ag in $\gamma$ /liter	
acetate	$\text{AgC}_2\text{H}_3\text{O}_2$	$1.04 \times 10^1$	$6.7 \times 10^5$	$1.82 \times 10^{-3}$
bromide	$\text{AgBr}$	$8.4 \times 10^{-5}$	$4.82 \times 10^1$	$4.1 \times 10^{-13}$
carbonate	$\text{Ag}_2\text{CO}_3$	$3.2 \times 10^{-2}$	$2.49 \times 10^1$	$6.15 \times 10^{-12}$
chlorate	$\text{AgClO}_3$	$1.0 \times 10^2$	$5.6 \times 10^7$	
perchlorate	$\text{AgClO}_4$	$5.25 \times 10^3$	$2.62 \times 10^9$	
chloride	$\text{AgCl}$	$1.5 \times 10^{-3}$	$1.13 \times 10^3$	$1.56 \times 10^{-10}$
citrate	$\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$	$2.8 \times 10^{-1}$	$1.76 \times 10^5$	
cyanide	$\text{AgCN}$	$2.2 \times 10^{-4}$	$1.77 \times 10^2$	$2.2 \times 10^{-12}$
fluoride	$\text{AgF}$	$1.82 \times 10^3$	$1.54 \times 10^9$	
iodide	$\text{AgI}$	$3.0 \times 10^{-6}$	1.38	$3.2 \times 10^{-16}$
nitrate	$\text{AgNO}_3$	$2.22 \times 10^3$	$1.42 \times 10^9$	
oxide	$\text{Ag}_2\text{O}$	$2.2 \times 10^{-2}$	$2.05 \times 10^4$	$1.52 \times 10^{-8}(\text{AgOH})$
orthophosphate	$\text{Ag}_3\text{PO}_4$	$6.5 \times 10^{-3}$	$5.02 \times 10^3$	
sulfate	$\text{Ag}_2\text{SO}_4$	5.7	$3.94 \times 10^5$	
sulfide	$\text{Ag}_2\text{S}$ (acanthite)	$1.4 \times 10^{-4*}$	$1.22 \times 10^2$	$1 \times 10^{-49}$ to $10^{-51}$
	$\text{Ag}_2\text{S}$ (argentite)	(insoluble)		
tartrate	$\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$	2.0	$1.17 \times 10^6$	

\*O. Weigel, quoted in Landolt-Börnstein, 5th ed., I. Suppl., p. 250, found a solubility of 1.74 g/liter, whereas the solubility product indicates a solubility of  $4 \times 10^{-9}$  g/liter. The difference may be explained by the tendency of  $\text{Ag}_2\text{S}$  to go into colloidal dispersion (A).

†1  $\gamma$  = 1 microgram =  $10^{-3}$  milligram =  $10^{-6}$  gram.

electrolytic current for the dispersion of the metal in the liquid. This method is used commercially in the Electro-Katadyn and Matzka processes.

It may be mentioned here that the local electrolytic polarization appears to give an explanation for the experience of several authors,<sup>10</sup> chiefly of Tammann and Rienäcker,<sup>3</sup> that the addition of another metal increases the oligodynamic activity in some cases and fails in others. If metal combinations of considerable differences of electrochemical potentials are used, the explanation for the increased activity is trivial.

For only a few metals, however, can one be certain of having an effect due to Ag, on account of its extreme position in the potential series, *i.e.*, most less noble metals will "protect" Ag and will go into solution themselves. For this reason Au was used<sup>3</sup> and it proved to cause an *increased* Ag activity if admixed in powder form (local elements), whereas it *decreased* the activity when dissolved in Ag as alloy, for complete inter-metallic solutions do not produce local potential variations. In fact a passivation of Ag by Au should be expected, resulting in a decrease of activity. As an example of the consequences of such conditions the observation of Egg<sup>4</sup> may be mentioned. This author reports a decrease of solubility of Ag to one-fourth in the presence of Cu.

Concerning the dispersion of the metal by an electrolytic current it has not been possible to obtain a picture of the physicochemical process which is entirely free from contradictions. As far as the purely chemical activation is concerned it appears certain that only the solubility of the compound formed at the metal surface determines the activity. If, *e.g.*, a silver surface is activated by means of Cl one will obtain an oligodynamic activity equivalent to an Ag concentration which corresponds to the solubility of AgCl. If the activation is produced electrolytically in pure water, oxides, carbonates, etc., will be formed, and the activity will then be equivalent to the resulting solubility. A list of the solubilities and solubility products of the more common monovalent silver salts is given in Table 1, which shows that with the exception of AgNO<sub>3</sub> the Ag concentration can under normal conditions not exceed  $10^{-2}$ – $10^{-3}$   $\gamma$ /liter.

If the silver ion is, however, brought into solution by an *electrolytic current*, one can produce silver concentrations which are far above the solubilities of any known silver compound possible under the circumstances. Although the Ag concentration may remain unchanged, the solutions should nevertheless be considered metastable; this is indicated by the occasional change into blue and brown colors, which indicate colloidal dispersion of the metal. Ultimately the metal is precipitated. In such cases, where large concentrations of Ag are dissolved in water, it appears difficult to assume the metal to be in a completely ionized state, as no anions can be accounted for in concentrations sufficient to have the solution at the necessary electrochemical equilibrium.<sup>21</sup>

The fact, furthermore, that these solutions are decidedly unstable suggests the assumption that the metal in such solutions is not fully dissociated but exists in a state of molecular dispersion, *i.e.*, the system is a hydrosol, which is only partly ionized. If the ion concentration is decreased by adsorption on organocolloids, etc., or by dilution (Katadyn process, *cf.* below) more Ag<sup>+</sup> are produced from the sol. The possibility of producing Ag hydrosols by electrolysis from silver electrodes has been proved by several authors<sup>12</sup> as well as the existence of a variation of Ag<sup>+</sup> concentration within unprotected Ag hydrosols with the concentration of the sol, which has been shown by Voigt.<sup>13</sup> For practical purposes, the particular state of the metal in the aqueous solution is probably unimportant. The

practical advantage of the electrolytic method of charging water with metal lies, of course, in the ability to produce very concentrated solutions without the presence of high concentrations of anions which, particularly in the case of silver, could be deleterious when used for disinfection or preservation of food materials.

Concerning the *duration* of the activity of an oligodynamic source, due consideration of the medium within which the test is made has to be given. Experience with liquid nutrients shows, in fact, that it is necessary to reactivate the oligodynamic sources sooner or later, for the process does not seem to be self-perpetuating as far as metallic sources are concerned. From experiments on solid agar plates no conclusion as to the duration of the activity can be drawn for the following reason: due to the high viscosity of solid agars, no convection can take place in the medium; consequently the ion distribution in the agar is entirely due to diffusion<sup>14</sup> (A). A concentration gradient will thus be established across the plate. The concentration is equivalent to the saturation near the active source, and decreases with the distance from the latter. The border of the sterile domain is situated at a distance where the concentration can be tolerated by the cells under the particular conditions of growth, nutrient, etc., each of which may considerably affect the local ion concentration, and presumably also the physiological effect of the organisms. Consequently, the degree of activity can be measured by the width of the halo, but only for exactly identical culture media and organisms. Furthermore, experiments on liquid nutrients cannot be compared with those on solid ones, as here the smaller viscosity permits convection and thus a fairly uniform ion distribution over the whole volume, so that gradients are absent. This explains the experience that the oligodynamic activity of a substance depends considerably on the type of substrate.

In this connection another property of oligodynamic substances may be briefly discussed as far as the physicochemical side is concerned, i.e., the *stimulative effect* on organisms exposed to weak oligodynamic activities. Numerous authors have reported that if the metal concentration is not sufficient for lethal effects, a stimulation occurs. This phenomenon is apparent in the growth distribution on the border of the sterile domain on agar plates (see Figures 1 to 5), inasmuch as the latter has a sharp dark border, which appears to indicate a denser growth. Closer investigation shows, however, that this border is due to a local extension of the very dense growth of *E. coli* at the agar surface, (obviously due to aerobic conditions) into the depth of the nutrient layer. Figure 6A shows a micrographic top view of the border region, 6B a view of a vertical section through this region in dark-field illumination, so that the colonies appear appear white on a dark background.

Figure 6A shows the border to be quite sharp, but closer inspection under a microscope reveals a somewhat increased size of the colonies at the border and a smaller number per unit area. This can be interpreted

as the consequence of a larger quantity of nutrient available on account of fewer survivors. The main effect is, however, the small zone of apparently aerobic growth into the depth of the agar (see schematic growth profile, Figure 6C). It suggests that the "stimulation" is due to oxygen ions which diffuse from the (oxygen-activated) source with the silver into the agar. At a distance where the Ag concentration is not lethal any more (border of sterile domain), the oxygen concentration is still sufficient to produce aerobic growth. This growth zone is restricted to a narrow region because the oxygen, being thus absorbed, cannot permeate

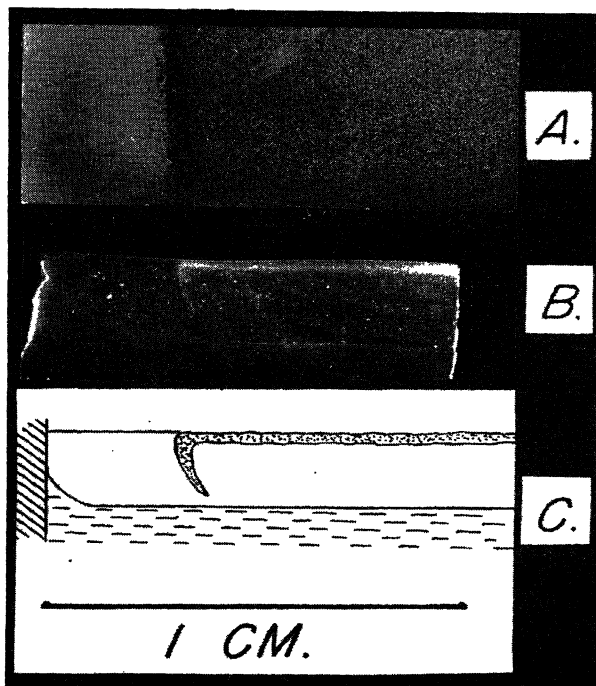


FIGURE 6. Growth distribution at the border of the domain sterilized oligodynamically: "A", micrographic top view; "B", micrograph of vertical section in dark-field illumination (the aerobic growth appears white) (about 6 diam.); "C", schematic profile of aerobic growth.

further into the agar. The zone, if seen from above, gives the misleading impression of a border region of increased growth density. If this interpretation is correct, the effect cannot be attributed to a truly stimulating effect of the metal (A). A somewhat similar interpretation has been given by Schumacher.<sup>15</sup>

From the foregoing discussion the following picture appears to be a description of the fundamental physicochemical aspects of the oligodynamic activity. In order to observe an oligodynamic action it is necessary that the metal go into aqueous solution. Aside from the possibility of using soluble metal compounds, the same effect can be produced

- (1) whenever minute traces of compounds are formed at the metal surface;
- (2) due to local potentials caused by deformation or by the presence of other metallic components in the source;
- (3) by straight electrolysis.

It is important that the dissolved compound be to a certain degree ionized. This necessity is proved by the inactivity of  $\text{Ag}_2\text{S}$  which, though not of negligible solubility, yet has practically no ionization (see Table 1) in contradistinction to, *e.g.*,  $\text{AgI}$  which is active<sup>16</sup> in spite of a very much lower solubility.

It is probably for the same reason that Ag bound to proteins is inactive, provided that the concentrations are not too large. Consequently, very much more metal is required for germicidal purposes in the presence of organocolloids. The same is true for any surface exposed to an active liquid, as the dissolved metal loses its activity when adsorbed, until an equilibrium state is reached between the surface and the liquid.

Beyond solubility and ionization of the compound, the anion plays no obvious role in the activity within the range of oligodynamic concentrations; it even appears that it is not necessary to introduce anions into the solution if an electrolytic method is used.

### III. THE BIOLOGICAL NATURE OF THE OLIGODYNAMIC EFFECT

Although it is well established that the oligodynamic action of certain metals, particularly silver, is able to affect widely different biological systems, namely crustaceans, protozoa, tissue cells of mammals, fish, plants, algae, fungi and bacteria, it is the last which have been studied to the largest extent. Primarily these studies are concerned with the conditions under which the oligodynamic effect occurs; they are treated here in the following order: temperature;  $\text{H}^+$  concentration; minimum lethal Ag concentration (lethal cell-ion equivalent); variation with species; microbial adaptation.

It is a general experience that the viability of bacterial cells is markedly influenced by the temperature and by the  $\text{H}^+$  concentration in the substrate in which they are suspended. Likewise it has been observed that the velocity of disinfection is dependent upon both temperature and pH. Numerous investigations have shown that both of these factors also influence oligodynamic action on the cell.

Temperatures below 20 °C have been found to retard oligodynamic action,<sup>17</sup> whereas above 20 °C the activity is accelerated.<sup>18</sup> Contrary to this some authors<sup>19</sup> report that the oligodynamic effect is independent of

temperature. This discrepancy appears not to be serious in view of the dependence of the effect on numerous other factors which very often do not permit a comparison of the results of different authors.

Experiments in this laboratory have shown that temperature definitely influences the oligodynamic reaction. When *E. coli* was suspended in nutrient broth containing  $\text{AgNO}_3$ , it was found that the minimum lethal concentration was less at 40 °C than at 25 °C, (Table 2). The tests were

Table 2 (A).—Effect of Ag on *E. coli* in Nutrient Broth at Different Temperatures.

Ag added	Concentration of cells per cc	Temper (°C)	Concentration of Ag in $\gamma$ /liter						
			320	640	1300	2500	3200	3800	5100 0.00 (con- trol)
Before inoculation	+10 <sup>5</sup>	40	+	+	+	+	—	—	+
	+10 <sup>5</sup>	25	+	+	+	+	+	+	+
After inoculation	+10 <sup>5</sup>	40	+	+	+	—	—	—	+
	+10 <sup>5</sup>	25	+	+	+	+	—	—	+

based on the observation that the temperature at which cells and Ag ions contact is most important; therefore the technique followed was such that the cells were introduced into broth at a constant temperature either before or after the Ag solution was added.

They were allowed to remain in contact at this temperature for nearly 60 minutes; then the tubes were placed in an incubator at 35 °C. The readings were taken after 72 hours. The results show that the minimum lethal concentration of Ag at 40 °C is 30-40 per cent lower than at 25 °C.

Table 3(A).—Effect of pH on the Oligodynamic Action of Ag in Nutrient Cultures of *E. coli* and *Sacc. cerevisiae*.

Test Micro- organism	Concentra- tion of cells per cc	Concentra- tion of Ag in γ/liter	—H <sup>+</sup> ion Concentrations (pH)—													
			3		4		5		6		7		8		9	
			Time in Hours													
<i>E. coli</i>	10 <sup>5</sup>	640	20	72	20	72	20	72	20	72	20	72	20	72	20	72
		1300	0	0	—	—	+	+	+	+	+	+	+	+	+	+
		2500	0	0	—	—	—	—	+	+	+	+	—	—	—	—
		3800	0	0	—	—	—	—	—	—	—	—	—	—	—	—
		5100	0	0	—	—	—	—	—	—	—	—	—	—	—	—
		000	0	0	+	+	+	+	+	+	+	+	+	+	+	+
<i>Sacch. cerevisiae</i>	10 <sup>5</sup>	640	—	—	—	+	+	+	+	+	+	+	+	+	—	+
		1300	—	—	—	+	+	+	+	+	+	+	+	+	—	+
		2500	—	—	—	+	+	—	—	—	+	+	—	—	—	—
		3800	—	—	—	+	+	—	—	—	—	—	—	—	—	—
		5100	—	—	—	+	+	—	—	—	—	—	—	—	—	—
		000	—	+	+	+	+	+	+	+	+	+	+	+	—	+

Tests (A) designed to show the effect of pH on the oligodynamic activity of silver were made with both *E. coli* and *Sacch. cerevisiae*. The cells were suspended in nutrient broth which had previously been adjusted to a definite H<sup>+</sup> concentration, with dilute H<sub>2</sub>SO<sub>4</sub> or NaOH,

and sterilized at 10 pounds steam pressure for 20 minutes. In the case of yeast cells the various concentrations of  $\text{AgNO}_3$  were added to the medium before inoculation, and 0.25 cc of approximately 25 per cent sucrose solution were added immediately afterward. These mixtures were made at  $25^\circ\text{C}$  and were at once placed in an incubator at  $35^\circ\text{C}$ . Readings were taken after 20 hours and after 72 hours. The results are given in Table 3.

The data show that the maximum resistance of *E. coli* reaches from pH 7 to 8. For  $\text{pH} < 7$  or  $> 8$  the quantity of Ag effecting sterilization rapidly decreases. It is interesting to note that the minimum lethal Ag concentrations at pH 9 and 6 are equal. At pH 5, only 640  $\gamma$ /liter Ag sterilize the culture. Since the control cultures showed equally vigorous growth over the entire range of pH tested, it is apparent that disinfection was favored equally by either acidity or alkalinity (see pH 6 and 9). This suggests that the pH variation influenced the resistance of the bacterial cell and in this way indirectly increased the germicidal powers of the Ag ions.

In the case of the yeast cells a similar explanation may also be valid. The optimum region of pH (4-5) for growth and physiological activity, corresponds to the region of maximum resistance to Ag. It is noteworthy, however, that more rapid growth occurred in cultures ranging from pH 6-8 where enhanced germicidal action of Ag developed. At pH 3, Ag in a concentration of 640  $\gamma$ /liter was lethal. The data certainly indicate that at high acidities disinfection is rapidly enhanced; also that it progressively increases with increasing alkalinity in regions more basic than the optimum  $\text{H}^+$  concentrations.

These results are also borne out in tests with fresh orange juice (Table 4). Dilute NaOH was added to orange juice to vary the pH. It

Table 4 (A).—Effect of  $\text{H}^+$  Concentration on the Sterilization of Orange Juice by Ag.

Test Micro-organism	Temp. ( $^\circ\text{C}$ )	Treatment with Ag	Vols. of Orange Juice (cc)	Time (hours)	$\text{H}^+$ Concentration (pH)				
					3.5	4.5	5.5	6.7	7.3
Natural contamination of fresh orange Juice	30	No	12	20	+	+	-	+	+
	30	Yes	12	20	+	+	+	+	+
	30	Yes	12	20	+	+	+	-*	-

\*Tubes showing negative at 20 hours fermented actively after 36 hours except the control tube for pH 5.5.

was then placed in small sterile flasks containing an inert carrier impregnated with active oligodynamic Ag metal. The tubes were placed in a shaking device maintained at  $30^\circ\text{C}$  and were connected to manometers by small rubber tubings. After 20 hours the results showed that orange juice with an acidity greater than pH 6.7 was actively fermenting, although at pH 6.7 and 7.3 no gas evolution had occurred. Fermentation occurred in these tubes, however, after 40 hours incubation. In these tests sterilization was not produced; however, bacteriostasis by

oligodynamic Ag was manifested in regions more alkaline than the optimum pH range for microbial growth and physiological activity. These results are in agreement with previous findings.<sup>20</sup> Some other authors, however, found that variation of pH had no influence.<sup>21</sup>

The *minimum lethal concentration* of oligodynamically active silver definitely depends upon the nature of the substrate in which the test is made as well as upon the nature and concentration of the test micro-organism. Sporulating bacteria are extremely resistant to oligodynamically active solutions by virtue of their spores. However the vegetative forms of these bacteria are no more resistant than other bacterial types. For example, when a 72-hour old agar culture of *B. subtilis* was added (A) to distilled water containing  $50 \times 10^3$   $\gamma$ /liter of Ag in a concentration of approximately  $10^5$  cells per cc, the spores remained viable for 72 hours

Table 5.—Minimum Lethal Concentrations of Ag<sup>+</sup> for *E. coli* in Nutrient Broth.

Concentration of cells per cc	Concentration of Ag in $\gamma$ /liter	Total No. Tests	No. Tests not Sterile	No. Tests Sterile	Apparent Min. Lethal Concentration of Ag in $\gamma$ /liter
$10^2$	640	2	2	0	
	1300	4	2	2	
	1900	5	1	4	1900
$10^3$	1900	5	3	2	
	2600	7	2	5	
	3200	7	2	5	2600
$10^4$	2500	2	2	0	
	3200	6	2	4	
	3800	3	0	3	3200
$10^5$	3200	6	4	2	
	3800	4	1	3	
	4500	4	0	4	3800
$10^6$	3800	5	4	1	
	4500	5	1	4	
	5100	2	0	2	4500
$10^7$	5100	3	3	0	
	6400	2	1	1	
	7000	2	0	2	6400
$10^8$	9600	1	1	0	
	11200	1	0	1	11200

at 35 °C. Longer periods were not tested. Similar results were obtained when the pores were inoculated into nutrient broth containing  $50 \times 10^3$   $\gamma$ /liter Ag; however, no growth occurred in these tubes, indicating that the spores were prevented from germinating by the silver or were destroyed as they germinated. These results agree with those of other authors.<sup>22</sup>

On the other hand, *E. coli* in a concentration of approximately  $10^4$  cells per cc, was killed in distilled water in 24 hours at 35 °C by 50  $\gamma$ /liter Ag, and 25  $\gamma$ /liter reduced the population nearly to 5 per cent. Under similar conditions yeast cells (*Sacch. cerevesiae*) in a concentration of  $10^3$  cells per cc were killed by 45  $\gamma$ /liter. Subsequent tests have shown



that very much less Ag is lethal for yeast cells in water (*cf.* below). These values for the lethal concentration of Ag in water are in agreement with those of numerous workers<sup>23</sup> who agree that concentrations of 40-200  $\gamma$ /liter are sufficient to sterilize water contaminated with non-sporulating bacteria.

When *E. coli* was exposed to Ag in nutrient broth, the minimum lethal concentration was found to be nearly 100 times higher than in distilled water. This indicated that organic complexes of silver were

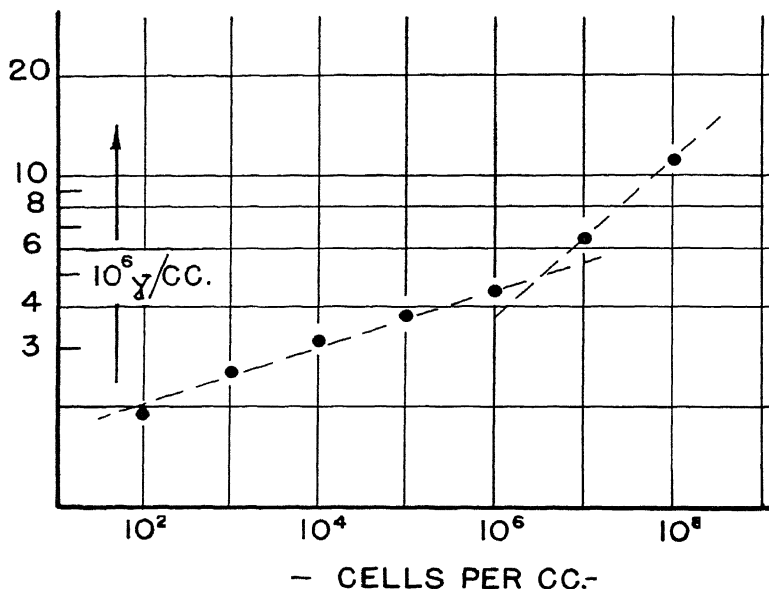


FIGURE 7. Minimum lethal silver concentration in  $\gamma$ /cc versus cell population (*E. coli*); both coordinates in logarithmic scale. The dashed lines represent two tentative (exponential) functions, demonstrating a "shielding" effect occurring for very large cell populations.

readily formed and that these compounds were not oligodynamically active. Determination of the lethal concentrations was based upon actual sterilization of the broth cultures after 72 hours incubation at 35 °C. The tests were made in the following manner: Dilute  $\text{AgNO}_3$  was added to the sterile broth tubes and thoroughly mixed at room temperature. Bacteria, diluted in nutrient broth, were then added and homogeneously dispersed throughout the silver solutions. The tubes were immediately placed in an incubator at 35 °C. The lag between addition of  $\text{AgNO}_3$  and cells was never greater than 10 minutes. The

results (Table 5) show that with increasing cell population, increasing concentrations of Ag are required to effect sterilization. However, approximately only 8 times more Ag was used to kill  $10^8$  cells per cc than was used to destroy  $10^2$  cells per cc (Figure 7). These values agree generally with the observations of various authors who studied the oligodynamic action of Ag in organic solutions.<sup>24</sup>

Table 6.—Summary of the Minimum Lethal Concentrations of Ag as Reported by Different Authors.\*

Min. Lethal Conc. Ag in γ/liter	Substrate	Time (hrs)	Test Micro-organism	Authors
1	H <sub>2</sub> O			Hoes
1.5	H <sub>2</sub> O			Pincussen
3	H <sub>2</sub> O			Dienert and Etrillard
20	H <sub>2</sub> O	20	<i>E. coli</i> ; pathogens	Viesohn
34	H <sub>2</sub> O		<i>E. coli</i> ; pathogens	Tauchert
			Gram + and gram - bacteria	
40	H <sub>2</sub> O	24	<i>E. coli</i>	Egg and Jung
50	H <sub>2</sub> O	3	<i>E. coli</i> ; <i>V. cholera</i> S. <i>paratyphi</i> ; Staph. <i>E. coli</i>	Metalnikoff
50	H <sub>2</sub> O			Herrmann
50	H <sub>2</sub> O; fresh orange juice			Callister
50	H <sub>2</sub> O; fresh orange juice	3-4	<i>E. coli</i> ; <i>E. typhi</i>	Kling
75	H <sub>2</sub> O		Water bacteria	Dimitriev
100-150	H <sub>2</sub> O	2.5	<i>E. coli</i> ; <i>Staph. aureus</i>	Myers and Mauer
100-200	H <sub>2</sub> O	3-5		Just and Szniolis
100-250	H <sub>2</sub> O	2-3	<i>E. coli</i>	Hoffman
250	Vinegar		Vinegar bacteria	Kreipe
260	Wash water for fruit, etc.	4	<i>E. coli</i>	Perini
260	H <sub>2</sub> O		Motile and nonmotile bacteria	Schioppa
130-300	H <sub>2</sub> O		Colon-typhoid bacteria	Rugge
25	H <sub>2</sub> O		Yeast	Luers
100	H <sub>2</sub> O		Wild yeast	
500	H <sub>2</sub> O		Sarcina	
40-900	H <sub>2</sub> O			Kul'skiĭ
500-1200	H <sub>2</sub> O		<i>E. coli</i>	Aleksandrov
1000	H <sub>2</sub> O		Staph.	Paterno and Masaniello
10 × 10 <sup>3</sup>	Serum; bouillon		<i>E. coli</i>	Gluck
5-20 × 10 <sup>3</sup>	Must; fruit juices		Yeast	Mehlitz
5-10 × 10 <sup>3</sup>	Fruit juice, vinegar		Yeast	Milla

\*For references of authors see bibliography, reference 26.

The rate of disinfection of oligodynamically active Ag in water or other substrates has been studied by numerous workers. Some of these investigations are summarized in Table 6. To demonstrate the dependence of germicidal action on time and Ag concentration the following experiments were performed (A) (Figure 8). Distilled water (10 cc) containing *E. coli* ( $10^5$  cells/cc) was sterilized in 4 hours, though over 99 per cent of the cells were killed in the first hour. The concentration

of Ag was constant at 130  $\gamma$ /liter. In tests containing 60, 130 and 640  $\gamma$  Ag/liter it was found that 60  $\gamma$  failed to sterilize the solutions in 18 hours although the tests containing 130 and 640  $\gamma$  were sterile in 8 hours and the bacterial count was reduced nearly 95 per cent in 1 hour. The inoculum in each test consisted of .01 cc of unwashed cells in nutrient broth.

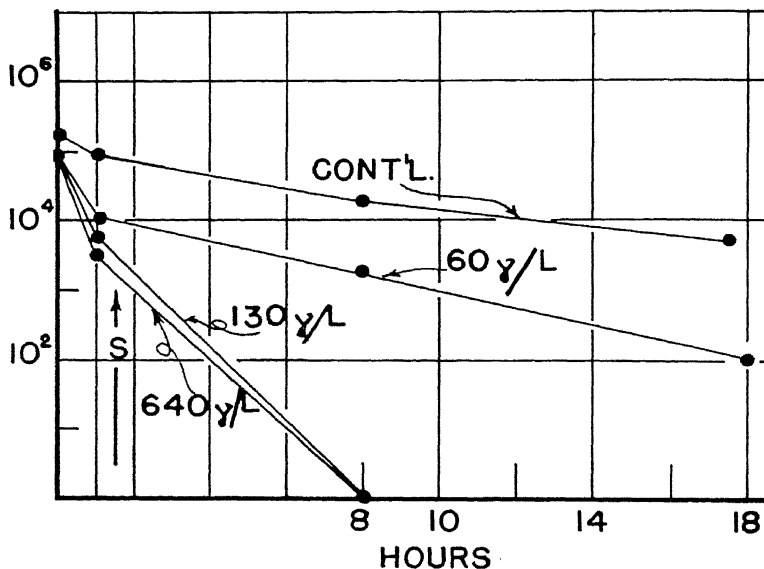


FIGURE 8. Disinfection *versus* time for different silver concentrations. The surviving population (S) (ordinate) is plotted on logarithmic scale. (The disinfection rate does not increase appreciably above 130  $\gamma$ /liters.)

Although the rate of disinfection for 640  $\gamma$ /liter appears to be slightly greater than that for 130  $\gamma$ /liter, this difference is small compared to the difference in concentration. This particular behavior suggests an interesting distinction between oligodynamic and normal disinfectants (A). The findings of other authors<sup>25</sup> appear to point in the same direction (800  $\gamma$ /liter not more effective than 260  $\gamma$ /liter, etc.).

As so far the minimum lethal concentration has been considered only from experiments which did not take into account the maximum possible efficiency of the silver present, one cannot arrive at a definite conclusion as to the actual magnitude of the "ion equivalent," *i.e.*, the number of ions necessary to stop the viability of the cell.

The ion equivalent can easily be calculated from the minimum lethal concentration as follows: if  $N$  is the population (number of cells) per cc,

$C$  the concentration of  $\text{Ag}^+$  in  $\gamma$ /liter, the ion equivalent,  $\nu$ —as 1  $\gamma$  contains  $5.6 \times 10^{15}$  Ag ions—can thus be determined by:

$$\nu = 5.6 \times 10^{15} \times 10^{-3} \times C/N$$

From the data given above it is found that  $\nu$  varies between  $10^5$  to  $10^7$ , depending upon the type of substrate used and upon the method by which the silver was added (see Tables 2, 6). It has been stated in the previous section that the ionized state of the silver is of fundamental importance for an oligodynamic effect; at the same time the experimental evidence seems to indicate definitely that Ag, once bound to organo-colloids, almost completely loses its ionized state. Thus if the activated water is added to the nutrient medium *before* inoculation, most of the  $\text{Ag}^+$  will be bound and therefore inactivated; whereas if it is added *afterward*, the probability that ions will touch a cell is considerably larger, though still very small in an absolute sense. Hence it is easily understood why  $\nu$  varies exceedingly with different techniques, and it is evident that for an absolute determination of  $\nu$  any possibility for an absorption of the  $\text{Ag}^+$  anywhere but on a cell has to be avoided.

Extended experiments along this line have been conducted in this laboratory and will soon be published in detail elsewhere. Hence only a brief account of the main results will be given here. In this work not only the strict avoidance of the presence of any colloidal substance (carefully washed cells in distilled  $\text{H}_2\text{O}$  under controlled pH conditions), but also the avoidance of adsorption on the walls of the containers is imperative. The more closely the fulfillment of these conditions is approximated, the lower is  $\nu$  found to be. For *Sacch. cerevisiae*, with which these experiments were performed, a rather complicated technique of mixing in paraffin vessels was worked out where pipettes as well as containers had been brought into equilibrium conditions for the minute Ag concentrations during several months. Under such conditions it was possible to obtain solutions in which silver concentrations of the order of  $10^{-6}$   $\gamma$ /liter could be kept for short times at an estimated accuracy of  $\pm 15$  per cent. Working with concentrations of this order of magnitude, it is possible to produce suspensions which have approximately the identical concentrations of cells and ions, as, for instance, 1 cc of  $10^{-6}$   $\gamma$  Ag/liter contains  $5.6 \times 10^6$  Ag ions, and it is easily possible to produce a suspension of the same concentration of yeast cells.

In order to obtain  $\nu$ , if it is a small number, it is necessary to know the statistical law by which the ions are distributed among the cells. Such laws are, however, mathematically worked out (*e.g.*, Poisson function, etc.) and have been incorporated. Figure 9 demonstrates the results thus obtained for the best possible initial mixing conditions. The number of dead cells ( $\Delta$ ) (established by direct count) is plotted versus the total number ( $N$ ) of cells present for a constant concentration ( $C$ ) of  $\text{Ag}^+ = 5.6 \times 10^6$  ions per cc. As the experimental uncertainty of the

value of  $C$  was estimated under the best possible experimental conditions to be  $\approx 15$  per cent, *i.e.*, to vary between  $4.6$  and  $6.5 \times 10^6$   $\text{Ag}^+$  per cc, this range is indicated by the dashed *horizontal* zone. The dashed *vertical* zone indicates the region within which the total number of cells present is equal to the total number of ions present.

The results show that under these conditions actually *only a single ion is necessary* ( $\nu=1$ ) for each cell to produce death, as the majority of the points fall within the zone. An obvious consideration of the scales used in Figure 9 shows that the possibility of  $\nu$  being larger than one (even for  $\nu=2$ ) is very remote. This outcome appears to be an interesting parallel to the unity of the quantum equivalent for the radiological cell death.

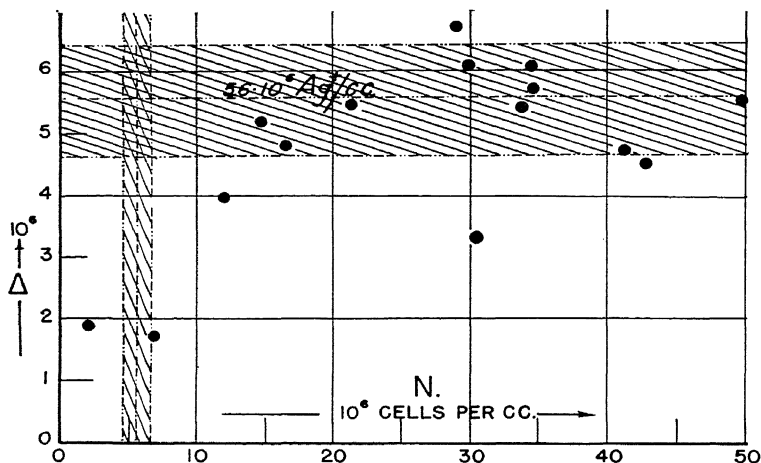


FIGURE 9. Number of killed cells/cc ( $\Delta$ ) versus total number of cells/cc ( $N$ ) in solution of  $10^{-6}$   $\gamma/\text{cc}$  of  $\text{Ag}$ . ( $=5.6 \cdot 10^6$   $\text{Ag}^+/\text{cc}$ ).

The dashed horizontal zone indicates the region where, within the estimated experimental uncertainty ( $\approx 15\%$ ), the number of *dead* cells equals the number of ions. The vertical zone indicates the region where the total number of cells ( $N$ ) equals the number of ions. The experiments with varying population suggest that the ion equivalent  $\nu=1$ .

The necessity for extreme experimental precautions in creating the conditions for a nearly perfect ion distribution among the cells present serves at the same time as an illustration of the relatively large inefficiency of the usual methods by which the metal reaches the organism. Although it appears evident from Figure 9 that one  $\text{Ag}^+$  can kill a cell, the latter does not lose its capacity for absorbing a great many more ions;<sup>27</sup> hence it is thinkable that even for comparatively large  $\text{Ag}$  concentrations a small fraction of the total number of cells present is shielded. This shielding effect will be the larger, the larger the cell population;

consequently the minimum lethal concentration will be found to increase rapidly beyond cell concentrations where the shielding becomes important (Figure 7). Obviously organocolloids and dead cells will act in the same manner.<sup>27</sup>

Realizing this situation one can understand easily why different investigators met with varying success the problem of sterilizing colloidal liquids, such as milk, fruit juices, vinegar and broths, by oligodynamic methods. Herriman<sup>28</sup> and Petit<sup>29</sup> had no success in sterilizing milk and beer with Katadynized processes; however, other authors report successful sterilization or pasteurization of fruit juices, milk, vinegar, must and other organic solutions (see Table 6). Generally the concentrations of Ag required in these fluids are considerably greater<sup>30</sup> than those used in water sterilization. Experience in this laboratory has been that orange juice, grapefruit juice or grape juice, either fresh or pasteurized by heat and experimentally inoculated with yeast cells, are seldom sterilized by Ag in concentrations varying up to  $25 \times 10^3$   $\gamma$  Ag/liter. Sterilization of pasteurized orange juice inoculated with  $10^3$  yeast cells per cc occurred with  $28 \times 10^3$   $\gamma$  Ag/liter, and  $16 \times 10^3$   $\gamma$ /liter disinfected the juice when the yeast population was approximately  $10^2$  per cc. Also it was observed that 640  $\gamma$  of Ag/liter delayed by 24 hours fermentation of orange juice containing  $10^5$  cells per cc. However, fruit juices seeded with approximately  $10^6$  yeast cells per cc could be sterilized at 40 °C only with Ag concentrations approaching 38–45  $\times 10^3$   $\gamma$ /liter. In fact, according to the experiments performed so far, temperatures ranging from 40 °C to 25 °C (5 °C intervals) failed to influence the concentration of Ag necessary to produce sterilization. Grape juice was more readily sterilized by Ag than the citric juices tested; however, in these experiments temperatures were also without significant influence on the lethal concentrations. In general  $20 \times 10^3$   $\gamma$ /liter was the order of magnitude necessary to prevent fermentation when the yeast population was  $10^5$  cells per cc.

Two biological properties which influence chemical disinfection in general are the *variable resistance* of species and the physiological capacity of *adaptation* to "normally" lethal concentrations of germicides. The latter property is commonly known as "fastness," and may be acquired suddenly or, as is usually the case, slowly through "training." It has been observed to occur in the presence of oligodynamic Ag in water<sup>31</sup> as well as in organic solutions. Feirer and Meader<sup>32</sup> cultivated a strain of *E. coli* in urine which grew readily in the presence of 100 or more minimum lethal concentrations of Ag. Moreover, a strain of *E. coli* was developed (A) which grew luxuriantly in nutrient broth containing  $3.2 \times 10^5$   $\gamma$ /liter although the minimum lethal concentration of the parent strain was  $3.8 \times 10^3$   $\gamma$ /liter. At these high concentrations of Ag the media showed slight precipitates, which, however, were harmless to cell growth. The cellular sediment, after several days' incubation, turned black-brown in color. Nevertheless, the cells were viable, stained Gram negative and

developed the usual colony exhibiting a metallic green luster on eosin-methylene blue medium.

Bacterial species show variation of resistance to oligodynamic Ag in very much the same way as they do for other chemical disinfectants. It was found (A) that *S. enteriditis* was more resistant to Ag in nutrient broth than *E. typhi* or *E. coli*, but this difference was not exhibited in distilled water. *Staph. aureus* and *Lactobacillus plantarum* were equally resistant to Ag in glucose broth, but in distilled water *L. plantarum* was killed by 5 times less Ag. *Staph. aureus* was slightly more resistant than *E. coli* under the same conditions.

Generally it has been found<sup>33</sup> that Gram positive bacteria were more sensitive than Gram negative, excluding the spore formers, and also<sup>34</sup> that pathogenic bacteria were less resistant to oligodynamic Ag than non-pathogenic microorganisms. The indefiniteness of the latter statement is illustrated by the contradictory observations of other authors<sup>35</sup> for water and organic solutions.

There is also complete disagreement concerning the sensitivity to oligodynamic influence in the case of the acid-fast bacteria, especially for the non-pathogenic varieties.<sup>36</sup> Although numerous investigators have recognized marked variations in sensitivity of bacteria even within a single bacterial strain,<sup>37</sup> no critical examinations of this biological phenomenon have been made.

Undoubtedly the previously discussed differences in media, pH, temperature, cell concentration, etc., may account for many of the discrepancies; however, it seems that the physiological behavior of the cells must also play an important role. This appears to be particularly true in view of the finding<sup>38</sup> that proteolytic bacteria are generally more resistant than saccharolytic types.

#### IV. PRACTICAL APPLICATION OF OLIGODYNAMIC ACTIVITY

The peculiar nature of the oligodynamic effect suggests various ways of utilizing it practically for the purpose of sanitation, sterilization, etc. As mentioned before, silver is preferable to other metals for such purposes whenever the material treated is to be used for human or animal consumption, because of the extremely slight solubility of most silver salts.

In fact, a number of methods have been elaborated in the past and have been used during the last ten years extensively in a variety of fields, particularly in Europe and Asia. The most widely used method is known under the name of "Katadyn" initiated by G. A. Krause, in Germany.

The Katadyn process uses two different methods for bringing active silver into solution: one consists in impregnating a neutral substrate which exposes a large surface (sand, bolus, gravel, silica gel) with small quantities of silver, which is then activated by various methods. Hence a material of comparatively small cost is obtained which will dissolve

silver in water whenever the latter comes in touch with it. By proper methods it is possible to obtain fairly long-lasting activities. Figure 10 gives a schematic view of such an arrangement which is used for the disinfection of drinking water and which replaces successfully other disinfectants or the necessity of boiling. It represents chiefly a pressure filter, where the water permeates a porous "candle," the interior of which is filled with activated sand. The rate at which the water flows through the candle determines its content of silver up to an upper limit of about 50  $\gamma$ /liter. This water can then be directly consumed.

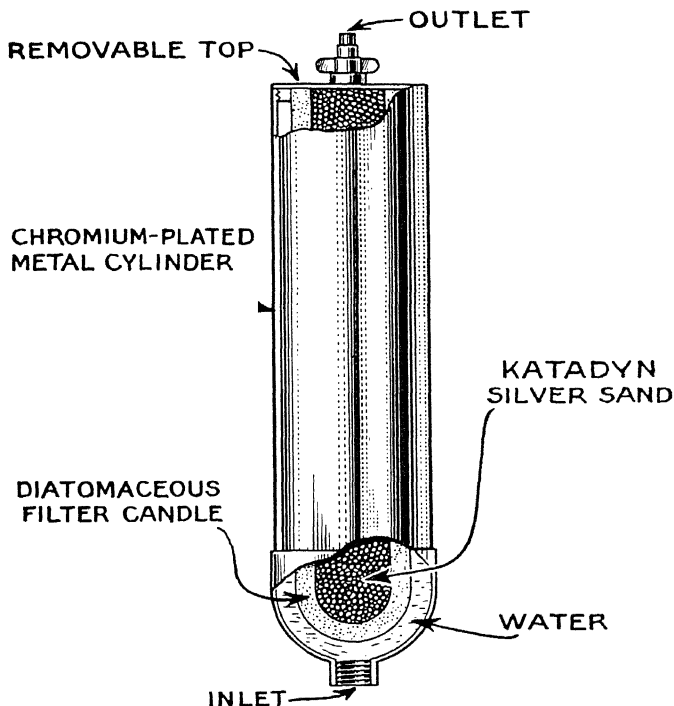


FIGURE 10. Oligodynamic water filter "Katadyn."

The other process is known as "Katadyn-Electro," and utilizes the previously described method of forcing metal by electrolysis in high concentrations into aqueous liquids. The apparatus consists chiefly of either a single pair or a large system of silver electrodes which are operated by direct current of about 1.5 volts. The water passes in a steady flow between the electrodes and thus continuously carries metal away.



The silver concentration is controlled by the regulation of the current; however the dissolved amount cannot be calculated directly from Faraday's law as the equivalent varies with the nature of the liquid for the reasons previously given. The actual yield is, for pure water, only about 50 per cent of the equivalent; it is even less for vinegar and fruit juices. The exact ion concentration can be determined by means of potentiometric methods,<sup>4</sup> the total Ag content by microanalysis. Concentrations of 50-2000  $\gamma$ /liter are used for such sterilizing processes, depending upon the material treated.

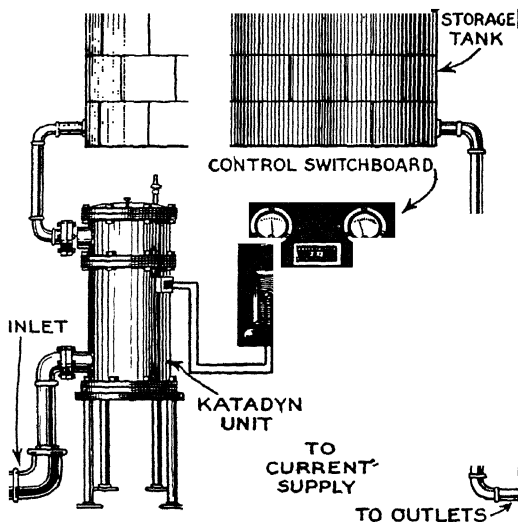


FIGURE 11. Arrangement for oligodynamic sanitation of a water supply system by electrolytic activation with "Katadyn-Electro" process.

As the metal goes into solution from the anode, and as, furthermore, most of the impurities and the anions of dissociated compounds in the water will be deposited on the anode, the latter will soon be inactivated by the formation of insoluble compounds. This is avoided by an arrangement which reverses the current in equal time intervals. Hence the cathode becomes the anode and the former anode is electrolytically cleaned.

Though the process gives considerably higher concentrations of silver (*cf.* above), the necessity for the electric equipment confines its use to applications where large quantities of liquids are to be treated, as in the sanitation of swimming pools, or in the treatment of water supplies

where the activated water is added to the large bulk in order to produce there the required (smaller) Ag concentration. Figure 11 presents the scheme of an arrangement for sterilization of a water supply system.

These silver solutions have been found to be very effective on pathogenic water-borne bacteria such as *E. typhi* (abdominalis), *B. paratyphi A*, *B. paratyphi B*, *S. dysenteriae* (Shiga), and *S. paradyserteriae* (Flexner), *B. cholerae* (asiaticae), *Staphylococcus aureus*, *E. coli*, and others. It is considered ineffective on spore-forming bacteria and some of the non-pathogenic bacteria, such as *Alcaligenes bookerii*, *Sarcina lutea*, and *Micrococcus aurantiaca*, have shown a tendency to develop a tolerance for silver. From a sanitary viewpoint they are admittedly of no significance and their growth in excessive numbers can be prevented by the occasional addition of small chlorine concentrations (Katadyn patent No. 2,018,916). The process is also effective in controlling the growth of slime and algae, and extensive work with rinse water used in breweries and dairies has shown a marked action on yeast, lactic acid bacteria, sarcina, acetic acid bacteria and other microorganisms deleterious in brewery and dairy operations. The sterilization of water by such methods is particularly important for military purposes, etc., in the tropics, and was, for instance, very successfully applied during the Italian campaign in Ethiopia. In other aqueous liquids Katadyn has been used to impede the growth of vinegar mother (*Bacterium xylium*) and eels in white cider and wine vinegar, and to prevent the fermentation of fruit juices. Low-grade wine has been freed from bacterial cloudiness and improved in its keeping qualities, and work on milk and beer has indicated a possibility of reducing the pasteurization temperature when applying the Katadyn silver treatment. Furthermore, the admixture of Katadynized water to meat pulp has been successfully applied in the manufacturing of ground meat products. Another very promising application appears to consist in the use of such water for the spray in air-conditioning systems.

Finally, it may be mentioned that this type of apparatus is also used for the production of the catalytic effect of dissolved silver upon the acid-ester ratio of alcoholic liquids and the consequent improvement of odor and flavor of raw alcohol.<sup>39</sup>

A different method for the introduction of silver into liquids such as fruit juices and wine is known as the Matzka method, which combines the empirically known increase of oligodynamic activity with temperature with the production of a source of electric energy necessary for the activation of the metal, by utilizing the thermoelectric force between a silver-gold alloy as oligodynamic anode and nickel or aluminum as neutral cathode.

As is evident from Figure 12 the electrodes are circular discs approximately two feet in diameter, piled on top of one another so that two plates of the same metal alternate with a pair of plates of the other metal (Ag-Ag: Al-Al: Ag-Ag, etc.). All plates are separated from one another

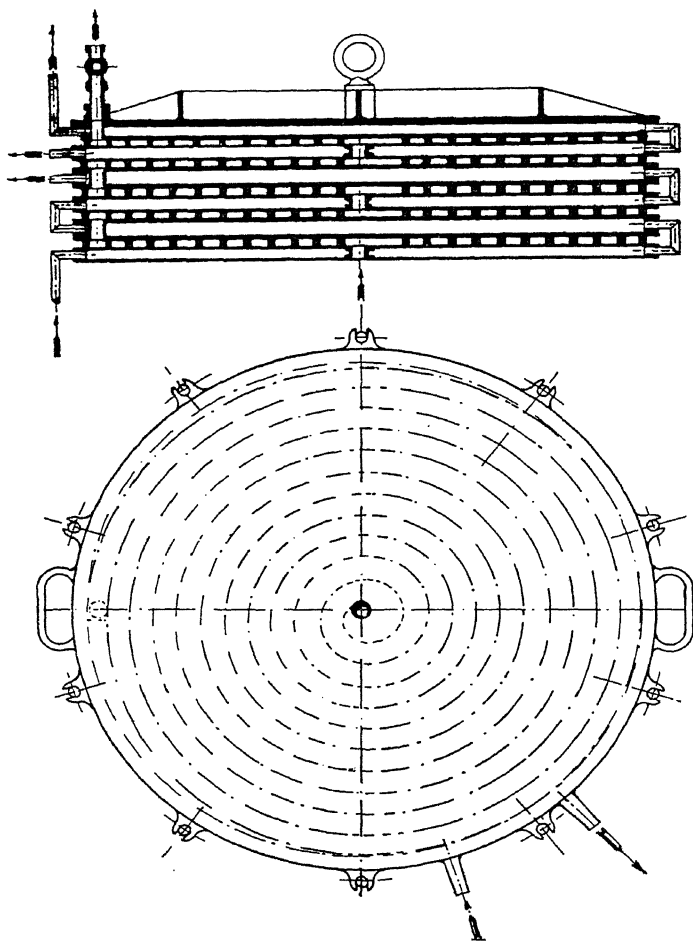


FIGURE 12. Apparatus for oligodynamic treatment of liquids by Matzka. The electrolytic activation is caused by thermo-electricity, which is produced by the maintenance of a temperature difference between plates of different metals (Ag and Ni). The liquid is forced through a series of helical channels (Matzka).

in such a manner that the interstices between two plates of the same kind are kept apart by a ring of conducting material, whereas the space between two different plates is filled by a spiral of an insulating flat rubber band, permitting a spiral channel between these plates running from the center to the periphery. These channels, sandwiched between different elements, are connected in series and the liquid to be sterilized

is pumped through them. Thus the liquid is always on one side in touch with silver, on the other with aluminum. The space between the plates of the same metal is used for maintaining a certain temperature by the circulation of heated water. The arrangement is such that the silver plates are kept at a temperature 15 °C above the temperature of the aluminum plates, which are kept at room, or slightly higher, temperature. The different couples are connected with one another in such a manner that they form a thermoelectric battery where one-half of the circuit is given by the current of the liquid. A sterilizer consisting of 10 elements and a liquid path of 400 feet permit the sterilization of 50 gallons per hour. Units up to 1000 gallons capacity have been built, or are under construction. The advantage of this method over that of pasteurization is claimed to consist in the preservation of the antiscorbutic vitamin C in addition to maintenance of the natural flavors.

Although the Matzka method is obviously successful, the apparatus is rather complicated and its function not very apparent. It is difficult to decide whether or not the increase of temperature is necessary only for the production of thermoelectric currents or whether, and to what extent, the increase of temperature has physiological influences upon the organisms in the liquids treated.

Aside from the Katadyn and Matzka methods there are numerous other modes of practical application which have led to a voluminous patent literature, contained in the bibliography on the subject<sup>40</sup> and Siebeneicher.<sup>8</sup>

## V. GENERAL PROBLEMS OF THE APPLICABILITY OF OLIGODYNAMIC PROCESSES

In conclusion, the major problems involved in a large-scale application of oligodynamic processes for sanitation, sterilization, pasteurization may warrant a brief discussion.

The use of Ag for water supplies, for the preservation of certain fruit juices, vinegar, wine, beer, etc., has already been applied on a fairly large scale in Europe, and it has proved satisfactory and commercially practicable, since the Ag quantities involved are very small indeed. A critical consideration of various problems, which all methods of chemical disinfection have in common, seems thus not out of place. Most of them are relatively unimportant in a laboratory, but can assume significance in large-scale applications, such as microbial adaptation, variation of bacterial resistance, argyria, atopy, and the effects of Ag on nutrients.

Concerning the sterilization of water with Ag, one has to realize that there is a difference between the effects of Ag and, *e.g.*, heat. Whereas it has been found empirically that in the latter case the destruction of resistant bacteria, such as *M. tuberculosis* or *Cl. botulinum* render the existence of other pathogens improbable, this is not necessarily true for chemical disinfection in general; in the case of Ag, however, the

destruction of *E. coli* has not been found to be unquestionably indicative, e.g., for *S. enteritidis* and *Staph. aureus* (A). It appears that considerably more work has to be done to clear up these questions, not only by the usual cultural methods but also by animal inoculation, feedings with centrifuged sediments of treated cultures, etc., in order to be able to distinguish clearly between bacteriostatic and bactericidal effects.

Another factor complicating the safe application of oligodynamic processes for effecting "pasteurization" is the ability of certain bacteria to adapt themselves to live in amazingly high Ag concentrations<sup>32</sup> (A). Most of these adaptations are slow and probably unimportant for practical applications; however, "spontaneous" adaptations have also been observed (A).

Concerning the toxicity of Ag-treated nutrients to the higher forms of life, it is evident from the excellent treatise of Hill and Pillsbury<sup>41</sup> that the Ag concentrations required would not be a dangerous source of argyria even when widely applied for public use. There still remains the problem of the significance of an argyrial atopy, although Hill and Pillsbury were unable to find convincing evidence that individual susceptibility enters into the development of argyria; this however does not exclude the possibility of sensitization to Ag compounds, especially when repeatedly consumed. On the other hand, silver table utensils have been used for centuries without any untoward effects; furthermore, no evidence of undesirable consequences due to consumption of Ag-treated foodstuffs for extended periods of time, have been reported in Europe.

Concerning the deleterious effects Ag may have on nutrients, there is complete lack of information concerning such consequences of oligodynamic sterilization, which would be of particular interest for fruit juices preserved in this manner. It has been stated repeatedly that the preservation of the vitamin C content of fruit juices treated oligodynamically was particularly successful. Undoubtedly the Ag concentrations required for preservation, though higher than those needed for sterilization of water, are insufficient actually to cause changes in the nutrient values, with the possible exception of the different vitamins and other comparable essentials. Nothing appears to be known about Ag with vitamins, whereas an inactivation of enzymes by exposure to Ag solutions has been reported.<sup>42</sup> The necessity for better information concerning these questions is evident.

In spite of the incomplete knowledge of many details involved in a more general application of the oligodynamic activity of Ag, it appears safe to state that—provided that certain difficulties in application can be mastered—Ag is an almost perfect chemical disinfectant for substances in contact with humans and animals. In contradistinction to all other agents, Ag is practically insoluble in those compounds which can occur under practical conditions. Consequently, it is almost impossible for large Ag concentrations to occur in solution, in contradistinction to most other heavy metal compounds. Nevertheless, oligodynamic Ag is as toxic

to primitive forms as the most powerful chemical disinfectants, at least in the absence of colloids. In view of the relative harmlessness of Ag to humans and animals, it is thus possible to increase the margin between the dangerous doses for humans and the concentration necessary for sterilization further than for any other chemical disinfectant.

The obvious advantage of the practical insolubility of the Ag compounds in question causes, at the same time, the chief difficulty in its application for germicidal purposes in the presence of organocolloids—the problem of disinfecting with an almost insoluble disinfectant. The study of the variation of the ion-equivalent (*cf.* above) with the conditions under which the ions are brought into contact with the cell appears to suggest methods by which this could be done in a considerably more efficient manner. The possibility of the application of the oligodynamic qualities of Ag to the preservation of foodstuffs will probably depend on the successful development of such methods.

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## Chapter 17

### Silver as a Fungicide

By L. W. NIELSEN \* AND L. M. MASSEY †

#### INTRODUCTION

Certain chemical elements and their compounds exhibit marked toxic or deleterious activity toward living organisms. This toxic property has led to the development of a number of practical fungicides having as their active principle copper, sulfur, mercury and some other elements. Silver, likewise, exerts toxic action on the lower forms of life to a very marked degree, probably more so than any other element. The toxicity of silver has been known for a relatively long time, but in the past no intensive effort has been made to develop a practical fungicide in which it is the active constituent.

The toxicity of silver has been utilized extensively in human and animal pathology. In this field it has been shown that both the inorganic and organic forms of silver possess medicinal properties. Since the methods of controlling diseases in plants and animals differ in certain respects, it is doubtful that many of the studies in animal pathology can be directly applied in plant pathology. Many of the silver compounds used and the methods of treatment in animal pathology do, however, suggest possible approaches to its use in the control of plant diseases. Because of the very limited application to plant pathology of the practices employed in animal pathology, the writers have made no effort in the following discussion to review the literature dealing with the use of silver in human and animal medicine, but rather, they have endeavored to bring together all available literature at their disposal, augmented by their own researches dealing with silver in its various forms, as it has been studied in relation to plants and plant disease control.

For expediency in presentation this chapter has been divided into several sections. Each section is devoted to a discussion of some fungicidal property of silver or its behavior when used as a fungicide in various disease control practices. The scope of discussion in the several sections is limited because available data pertaining to silver and its use in plant disease control are meager. It is believed, nevertheless, that this summary of our present knowledge about silver as a fungicide will constitute a helpful starting point from which future researches may be directed.

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## TOXICITY OF SILVER TO PLANTS AND PLANT ORGANS

The sensitivity of the plant to the fungicide is one of the important factors which must be taken into consideration in treating plants for disease control. All plants are sensitive to toxic materials when the latter are applied at sufficiently high concentrations. A given species of plant may be more sensitive to a certain toxic element than another species, and a given plant species may be more sensitive to some compounds of a toxic element than it is to other compounds of the same element. Most of the higher plants, because of their anatomical structure, are usually less sensitive to toxic materials than the more simple plant forms such as fungi and bacteria. This difference in sensitivity of the susceptible and the pathogen makes it possible to control pathogenic diseases. When this difference is large for a given toxic material, the probability of controlling a specific disease is much greater than when it is small. Many plant diseases have not been satisfactorily controlled with our present fungicides because the difference in sensitivity as between susceptible and pathogen is very small. In these cases a concentration of the fungicide great enough to be lethal to the pathogen is injurious to the susceptible. After many years of experience in disease control with various fungicides, it has come to be known that certain species and genera of plants are "copper sensitive," "sulfur sensitive," etc. It is therefore of interest to know what plants are "silver sensitive."

At the present time it is impossible to list the species of plants which are most sensitive to silver, since its general use as a fungicide has never been developed. Observations have been made, however, which indicate that silver is not different from other toxic elements in the character of its toxic action on plants. Whether it is toxic to the same plant species as are the other elements and under the same conditions remains to be seen.

The dipping of seeds of several plant species in silver solutions for the control of plant diseases has disclosed some evidence of the toxic action of these solutions on the susceptible organs involved. Tobacco seed dipped for 15 minutes in a 1:1000 silver nitrate solution are less injured than tobacco seed given a similar treatment with other chemicals.<sup>4, 39-43</sup> The injury is increased if the duration of treatment is increased.<sup>4</sup> The 15-minute dip hastens the germination of tobacco seed and the development of the cotyledons and primary leaf, but the development of the root is retarded.<sup>56</sup> Barley seed dipped for 30 minutes in a 1.7 per cent silver nitrate solution are reported by Birckner<sup>57</sup> to be injured by the treatment. In other cases barley seed dipped in a 5 per cent silver nitrate solution for 18-24 hours showed no apparent injury,<sup>34, 58</sup> but in these cases the seed coats were unbroken. Rye and wheat seed have been similarly treated, with no injurious effects.<sup>58</sup> Wheat<sup>33, 38, 48</sup> and barley<sup>48</sup> seed dipped for shorter periods of time are not injured. Dosdall<sup>37</sup> reports an 11 per cent reduction for barley and a 2 per cent

reduction for wheat seed germination following an overnight treatment in 0.01*N* silver nitrate solutions. This reduced germination may have been due to injured seed coats. Schroeder<sup>34, 58</sup> has found that seed with broken seed coats are killed by the silver nitrate dip. The retardation of the germination of wheat seed has also been reported.<sup>47</sup> In addition, silver nitrate is toxic to the seed of peas,<sup>5, 35</sup> beans and several species of the *Cruciferae*.<sup>34</sup> In the case of peas this toxicity is associated with permeability of the seed coat to the silver nitrate.<sup>34</sup> Under field conditions the foliage and blossoms which develop from narcissus bulbs treated with silver solutions show no evidence of injury.<sup>51</sup> From the foregoing discussion it is obvious that silver solutions are toxic to the seed of certain plant species. In some species the injury is due to permeable seed coats, which permit the silver to pass through to the embryo, and in others, to broken seed coats. Injury in all cases is associated with the conditions under which the silver bath is applied and with the duration of treatment.

The injury to young seedlings by many chemical solutions has also been investigated. Seedlings with radicals only a few centimeters long have been suspended in solutions of toxic materials at various concentrations or planted in a sand substratum saturated with toxic solutions. Under such conditions silver is very injurious to seedlings of wheat,<sup>54, 59</sup> lupine,<sup>60, 61</sup> peas and corn.<sup>62</sup> Silver is less toxic than nickel but equals the toxicity of zinc and copper to seedlings placed in a quartz sand substratum saturated with chemical solutions.<sup>54</sup> The writers have found that tomato, cucumber, gypsophila and snapdragon seedlings growing in greenhouse soils are seriously injured when watered with solutions containing more than approximately 20 p.p.m. of silver. Silver nitrate mixed with soil in which geranium plants are growing is less toxic to these plants than compounds of certain other elements.<sup>63</sup> Silver, however, is especially toxic to very young seedlings. Fewer data are available on its toxicity to mature plants and their organs.

The writers have observed under laboratory conditions that silver nitrate solutions containing 1000 and 100 p.p.m. of silver when used as sprays are toxic to the leaves of young tomato plants 6 nodes in height, and to bean plants in the primary leaf stage of development. The injury is most apparent where the drops of solution have dried on the leaves. A silver-soap spray containing a high concentration of soap is injurious to the young spring foliage of grapes.<sup>28</sup> The writers have similarly observed that a silver chloride spray containing a wetting agent and those sprays prepared by admixing silver nitrate with sodium lauryl sulfate, and particularly sodium oleyl sulfate, are more likely to produce injury than other silver sprays. The silver-oleyl sulfate spray mixture has injured the sprayed plants on two occasions when tested under field conditions. The silver-lauryl sulfate mixture, on the other hand, has produced visible foliar injury on only a limited number of the plant species sprayed with it under field conditions. These restricted observations suggest that the use of wetting agents in silver sprays may intensify the toxic action of silver to

certain plant species. Two inorganic silver sprays containing no wetting agent caused a russetting of apple fruits under field conditions but no evident leaf injury.

The composition of the silver spray mixture may likewise determine whether it will injure certain plant species. Under greenhouse conditions a spray mixture containing silver sulfate, manganous sulfate and calcium hydroxide was non-injurious to sprayed potato plants. A similar spray mixture containing ferric sulfate in place of manganous sulfate was, however, injurious to the young potato leaves. Since a silver spray possessing the desired physical properties has not yet been developed, it is impossible to predict what plants will be sensitive to a practical silver protectant. It is highly probable, however, that certain plant species will prove to be more sensitive to silver than others.

#### TOXICITY OF SILVER TO PLANT PATHOGENS

Experimental work comparing the toxicity of silver with that of other metal poisons is very meager, particularly in the case of bacterial pathogens. Many bacteria have been shown, however, to be sensitive to silver. Raadsveld,<sup>1</sup> reviewing some of the literature dealing with the toxic action of metals and their salts, points out that silver is one of the most toxic elements to various species of bacteria commonly employed in bacteriological research. With respect to the bacterial plant pathogens, Keitt *et al.*<sup>2, 3</sup> found silver sulfate to be the most toxic of the chemicals tested on *Erwinia amylovora*. Johnson and Murwin,<sup>4</sup> using silver nitrate to disinfect tobacco seed contaminated with *Bacterium tabacum*, clearly show that silver equals mercury in toxicity to this organism. This information, although limited, on the relative toxicity of silver and other elements to bacterial plant pathogens is in agreement with that reported for many other bacteria. Spore-forming bacteria are evidently less sensitive to silver,<sup>5</sup> but since there are probably no spore-forming bacterial plant pathogens,<sup>6</sup> further researches would very likely prove many other pathogenic forms to be sensitive to very dilute silver concentrations.

The toxicity of silver to pathogenic fungi has been more extensively studied. Representative species of the Phycomycetes, Ascomycetes, Basidiomycetes and Fungi Imperfectii have shown marked sensitivity to its toxic action. In many cases the relative sensitivity of certain fungi to silver, copper and mercury has been determined; and since compounds of the last two elements are regularly employed for plant disease control, the relative toxicities of these elements will be pointed out in the following discussion.

Two basic methods have been employed in testing the toxicity of various compounds to fungi. By the first method the toxic substance is mixed in the medium upon which the fungus is grown. The media in these experiments have varied widely in composition and concentration. In the second method, possibly the more reliable for giving a true meas-

ure of the relative toxicities in a group of compounds, fungous spores are suspended in a dilute solution of the toxic substance and its effect on their germination observed. This method eliminates the difficulties introduced by the use of complex culture media. It has been shown that the lethal concentration of a given toxic substance varies with the composition<sup>7, 8</sup> and the concentration<sup>8</sup> of the nutritive medium. This altered toxicity for a given chemical is probably due to its adsorption on the organic colloids present or to incompletely reversible chemical reactions with the organic medium. Chemical reactions take place when the salts of heavy metals are placed in media containing proteinaceous materials. In these systems such heavy metals as silver and mercury probably replace the hydrogen of amino- groups, as has been pointed out by Davenport.<sup>9</sup> Other chemical reactions may likewise reduce the effective toxic cation concentration in these media, and the degree of removal of various metal cations from solution is probably not the same for each medium. One may, therefore, reasonably question the reliability of data on relative toxicity obtained from experiments in which the toxic substances were combined with a complex organic medium.

That silver is toxic to certain fungi in very dilute concentrations has been demonstrated by growing *Aspergillus niger* in a liquid medium held in silver culture dishes.<sup>10, 11</sup> The fungus growth in these cases was sub-normal to very feeble in comparison with similar cultures held in glass containers. The writers have observed that the conidia of *Sclerotinia fructicola* germinate very poorly or not at all in distilled water containing finely divided silver. This retardation in fungus development has been attributed to the dissolution of silver by the culture medium.<sup>10</sup> Bornard,<sup>11</sup> however, was unable to determine the presence of silver by chemical tests in liquid media which had been in contact with silver dishes for 10 days. The chemical tests which he employed were probably inadequate for the task, since Wernicke and Modern,<sup>12</sup> using a method which concentrated the silver, have shown that silver ions go into solution from a metallic silver surface. The toxicity observed in the culture media held in silver dishes was undoubtedly due to the dissolved silver ions.<sup>1</sup>

In a number of reported experiments<sup>13, 14, 15</sup> the toxic materials have been mixed with media having a relatively high colloid and protein content. In all cases silver was found to be less toxic than mercury, but more toxic than copper, to the various fungi grown on the media. The sensitivity of different fungous species to a given chemical was observed to vary considerably.<sup>15</sup> This variability in the sensitivity of living organisms is a commonly observed phenomenon. The degree of chemical and physical reactions between the components of the media and the added chemicals was not determined in these experiments and the concentration of the free silver is not known. Hence one may reasonably question the validity of the toxicity determinations in these studies.

Other workers have employed less complex culture media for toxicity

determinations. The media were composed of water extracts of organic materials; or small amounts of specific organic compounds were added to a solution of inorganic salts. Even with these liquid media one might expect an interference by the components with the lethal action of the added toxic chemicals. Clark<sup>16</sup> added toxic compounds to a sugar beet root infusion to which had been added the whites of eggs. Silver was found to be more toxic to two of the five species of fungi grown on this medium, and mercury was more toxic to two of them. Both were about equally toxic to the fifth. Raulin<sup>10</sup> added sugar and tartaric acid to a liquid medium which contained very small amounts of inorganic salts and then added toxic compounds to this medium. In these studies silver was toxic to *Aspergillus niger* at a concentration three times more dilute than mercury and several hundred times more dilute than copper. After standing several days, the fungus began to grow on cultures with dilute silver concentrations. This delayed growth, Raulin explained, is due to the silver being gradually reduced\* by the organic constituents of the medium. Burström<sup>17</sup> added various toxic compounds to water extracts of both horse dung and soil rich in humus. Under these conditions silver is more toxic than copper and equally as toxic as mercury to the chlamydospores of *Tilletia tritici*. From these observations it appears that the simplification of the culture medium has somewhat altered the apparent relative toxic action of the three elements. In each case silver was markedly more toxic than copper, and in general equal to mercury in toxicity.

In a few cases an effort has been made to eliminate as completely as possible all interfering chemicals from the toxic medium. Spore suspensions of various fungi have been placed in water solutions of the toxic compounds, and the subsequent germination of the spores as they were affected by the toxic materials was observed. Kotte<sup>18</sup> introduced sporangial suspensions of *Plasmopora viticola* directly into dilute solutions of chemicals and determined the minimum molar concentration which inhibited sporangial germination. Under these conditions silver is more toxic than either copper or mercury. McCallan and Wilcoxon<sup>19</sup> similarly placed the spores of four fungi, i.e., *Botrytis paeniciae*, *Pestalotia stellata*, *Uromyces caryophyllinus*, and *Sclerotinia americana*, respectively, in dilute solutions of many chemicals and determined the concentrations which permitted a given population of the spores to germinate. Silver was found to be 3 to 14 times more toxic to these four species than was mercury and 14 to 52 times more toxic than copper. Here the difference in sensitivity of different fungi to a given chemical is again demonstrated.

All silver compounds are evidently not toxic to fungi. The toxicity of silver is due to the presence in solution of free silver cations; there-

\*In translating, it was not clear whether he meant chemically reduced, or that the silver concentration was reduced (lowered) by adsorption or chemical combination with the organic materials.

fore, one might expect those compounds which are very insoluble, e.g., silver sulfide, and those which ionize very weakly, to be non-toxic or only slightly toxic. Clement<sup>20</sup> prepared several nutrient solutions containing principally the silver protein compounds collargol, argyrol and protargol, and in each case *Aspergillus niger* grew normally in them. The writers have also observed that silver nucleinate only partially inhibits spore germination of *Alternaria solani*. In these cases the lack of toxic action is probably associated with a low degree of ionization. In a following section of this chapter the writer presents data showing that the toxicity of silver salts, when tested as fungicides on leaves, is correlated with solubility. Raadsveld<sup>1</sup> cites literature pointing to the correlation of solubility with toxicity as observed with bacterial cultures.

It is clear from this discussion that silver is one of the most toxic elements to plant pathogens. In every case cited it has been more toxic than copper, and in some cases many times more toxic. With the more refined methods for testing the toxicity of fungicides, silver has been found to be more toxic than mercury. There are probably many pathogenic organisms which are relatively resistant to silver but sensitive to copper and mercury. The reverse is true for several forms already studied. The marked toxicity of silver toward some of the pathogens studied is indeed an encouragement to those who may try to develop a practical fungicide with silver as the active constituent.

#### SILVER AS A PROTECTIVE FUNGICIDE

The spraying of plants with chemical solutions or suspensions is one of the most widely used methods of disease control. This method has been practiced for many years, and as a result, innumerable chemical compounds have been tested as potential sprays and a few have successfully withstood the test of time. At present most sprays have either copper or sulfur as their basic toxic constituent. After spraying numerous economic plants with various compounds and forms of these elements for many years, it has become evident that none is wholly satisfactory under all conditions. It is therefore necessary that an effort be made to develop or discover chemical compounds of other elements which can be used to replace those now in use where they are known to give unsatisfactory disease control. Even though the study of chemical substances relative to their fungicidal properties has been extensive, there are still many additional chemical compounds which may be tested. Among these are silver compounds.

The factors which must be taken into consideration when attempting to develop a successful plant spray are multifarious. The physical, chemical and biological properties of the compound, the sensitivity of the susceptible and the pathogen to the compound, the many ecological, meteorological and solar factors all must be reckoned with in undertaking the development of a plant spray. It is little wonder that the method of

trial and error has been usually the successful one in developing fungicidal sprays.

It has been learned from experience that a successful field spray must possess a number of fundamental characteristics. Without further elucidation the following may be listed:

- (1) Toxicity
- (2) Adhesiveness
- (3) Stability and availability of the chemical
- (4) Ease of preparation and application
- (5) Economic practicability
- (6) Susceptibility

The want of any one of these characteristics may disqualify a chemical mixture which might otherwise be a satisfactory fungicidal spray.

Sprays are applied in disease control either as eradivative or protective agencies. The eradivative spray is applied to destroy a pathogen which is already present in or on the suscept. The protective spray is applied in anticipation of the later arrival of the pathogen. Protectants are more generally used, as it is frequently difficult to eradicate a pathogen without injuring the suscept. In the following discussion silver will be treated exclusively as a protectant. No experimental data are available relative to its use as an eradicant.

During the first ten to fifteen years of the present century several silver compounds and mixtures were tested under field conditions as protectants. A silver nitrate-soap mixture was most extensively studied. The field performance of this mixture was exceedingly variable, and the use of silver compounds as protectants fell into disrepute. The silver-soap mixture suggested by Vermorel and Dantony<sup>22</sup> contained 20 grams of silver nitrate and 300 grams of granulated soap in 100 liters of water. These workers reported satisfactory control of downy mildew of grapes with this spray mixture, as did Müller.<sup>23</sup> Later experiments by Müller, Kulisch (as cited by Hollrung<sup>24</sup>), and Labergerie<sup>25</sup> showed that the silver-soap mixture was unsatisfactory. It was suggested that the soap concentration be increased according to the degree of hardness of the water being used in preparing the sprays.<sup>26, 27</sup> Pantanelli,<sup>28</sup> using 1 kilogram of soap per 100 liters of spray, was able to control leaf and fruit infection of grapes caused by *Peronospora* or *Oidium*, but the yield of fruit was reduced. It was further suggested that copper sulfate and pyrogallie acid be added to the silver nitrate,<sup>29</sup> but no data are available as to the efficacy of this mixture in controlling diseases. An ammoniated silver chloride solution containing 106 to 133 p.p.m. of silver was also tested as a protective fungicide; this gave promising control of the gray rot of grapes caused by *Botrytis cineria*.<sup>21</sup> More recently silver nitrate has been found to be as effective as mercuric chloride in controlling brown-patch of turf.<sup>30</sup> These few data probably constitute most of those published on the use of silver as a protectant.

It need hardly be said that the studies made have been qualitative only, and have included a very few of the numerous organic and inorganic silver compounds.

The writers have endeavored to extend the experimental knowledge of the use of silver salts and mixtures as protectants. They have tested many of the common inorganic silver salts and some organic silver mixtures for their fungicidal (ability to inhibit or kill fungous spores) activity. Since it is difficult to resuspend relatively insoluble salts or materials and at the same time obtain uniform particle size and dispersion, the silver compounds and mixtures discussed in this section were freshly prepared at the time of testing. The nitrate salt has served as the original source of silver in most of the authors' experiments. The common inorganic salts were prepared by admixing a silver nitrate solution (0.0092*N*), with a slight excess of the anion (0.01*N*) with which it was desired to have the silver cation combine. The excess of anions peptized the precipitated silver salt, thus holding it in suspension in a finely divided state, and at the same time insured complete conversion of the silver to the desired salt. Silver-soap mixtures were prepared according to the formula suggested by Vermorel and Dantony.<sup>22</sup> Two granulated commercial soaps and a sodium salt of sulfonated lauryl alcohol were used.

The fungicidal action of the freshly prepared inorganic salts and silver-soaps was tested upon excised potato leaves. The surfaces of the potato leaves chosen for the experiments were wettable with water, thus insuring a complete wetting by the silver spray suspensions, many of which have a surface tension not appreciably different from that of water. The sprays contained 100 p.p.m. of silver and the potato leaves were sprayed until completely wetted. After drying, a spore suspension of *Alternaria solani* was placed on the sprayed leaf surfaces either dropwise or by atomizing. Spore germination took place at room temperature in glass moist chambers. After 18 to 24 hours the spores were removed from the leaf surfaces with a collodion smear<sup>31</sup> and mounted on glass slides for spore germination counts. Table 1 summarizes the data from a series of experiments in which the freshly prepared silver compounds were tested for their fungicidal action.

Under the conditions of these experiments not all the silver compounds were fungicidal. An examination of the data on solubility presented in the table shows that compounds which inhibit spore germination are salts which produce the highest silver concentration in a water solution. On the surface of excised potato leaves, the minimum silver concentration lethal to the spores of *Alternaria solani* is evidently between  $2 \times 10^{-4}$  and  $4.5 \times 10^{-5}$  gram of silver per liter. The silver-soap mixtures inhibited spore germination in every case. Silver nucleinate was exceedingly variable in its behavior. In all experiments some degree of spore germination took place. This variation is possibly associated



Table 1.—Germination of Spores of *Alternaria solani* on Excised Potato Leaves Sprayed with Various Silver Compounds and Mixtures.

Silver Compound	Spores of <i>Alternaria solani</i>			Solubility Grams of Silver per Liter at 20 °C
	Germinated	Not Germinated	Not Germinated (%)	
Control	442	25	5.4	
Silver arsenate	0	590	100.0	$^a 3.96 \times 10^{-3}$
Silver arsenite	0	660	100.0	$^a 5.56 \times 10^{-3}$
Silver carbonate	0	595	100.0	$^a 2.5 \times 10^{-3}$
Silver chloride	4	506	99.2	$^a 1.08 \times 10^{-3}$
Silver chromate	1	631	99.8	$^a 1.79 \times 10^{-2}$
Silver cyanide	0	568	100.0	$^a 1.77 \times 10^{-4}$
Silver dichromate	2	582	99.7	$^a 4.15 \times 10^{-2}$ (15 °C)
Silver phosphate	0	525	100.0	$^a 5.02 \times 10^{-3}$ (19.5 °C)
Silver nitrate	0	525	100.0	$^d 1326.9$
Silver oxide	0	569	100.0	$^d 4.68 \times 10^{-2}$ (25 °C)
<sup>a</sup> Silver chloride plus ammonia	0	591	100.0	
Silver bromide	359	624	63.5	$^d 4.46 \times 10^{-5}$
Silver ferrocyanide	340	32	8.6	
Silver iodide	263	373	58.7	$^d 1.53 \times 10^{-6}$
Silver sulfide	369	25	6.4	$^d 3.42 \times 10^{-17}$ (18 °C)
Silver thiocyanate	68	501	88.2	$^d 8.35 \times 10^{-5}$
Silver thiosulfate	390	111	22.1	
<sup>b</sup> Silver nucleinate	313	724	69.8	
Silver-lauryl sulfate	0	606	100.0	
Silver-Soap No. 1	0	390	100.0	
Silver-Soap No. 2	0	463	100.0	
Silver-oleate	0	341	100.0	
<sup>c</sup> Colloidal silver	0	506	100.0	

<sup>a</sup> Enough concentrated  $\text{NH}_4\text{OH}$  to dissolve silver chloride precipitate.

<sup>b</sup> Commercial product containing 19-22 per cent silver.

<sup>c</sup> Prepared by reducing 0.0092N  $\text{AgNO}_3$  with 0.01N  $\text{SnCl}_2$ .

<sup>d</sup> Calculated from data in "International Critical Tables."

<sup>e</sup> Calculated from data on solubility, "Handbook of Chemistry and Physics," 23rd ed., p. 1002, Chemical Rubber Publ. Co., 1939.

<sup>f</sup> Calculated from solubility product ( $1.6 \times 10^{-48}$ ).

with low ionization of the silver nucleinate and with variation in the sensitivity of the spores from different cultures of the organism to the silver.

It is evident from these experiments that some of the silver compounds and preparations yield a sufficient concentration of silver ions to be toxic to fungous spores when these are placed on plant tissue. Several of the compounds and mixtures which reduced spore germination to a minimum were tested under greenhouse conditions for the prevention of infection by specific pathogens. In the preliminary experiments the sprays were made to consist of solutions or suspensions of silver salts only, as a test of the toxicity of silver in the absence of adjuvants. Potted barley, bean and celery plants were sprayed with silver nitrate solutions for the control of *Erysiphe graminis*, *E. polygoni* and *Septoria apii*, respectively. Potted potatoes were sprayed with a silver chloride suspension for the control of *Phytophthora infestans*. The spray mixture in each case contained 100 p.p.m. of silver. Because of the heavy cutin on the barley leaves, it was necessary to add a wetting agent to the silver nitrate solu-

tion sprayed on these plants. Repeated applications were made from time to time on the barley and bean plants to protect the newly exposed leaf surfaces, since the spores of the two pathogens were present at all times in the greenhouse. A single application was made on the celery and potato plants followed, after drying, by an artificial inoculation with a spore suspension of the respective pathogens. In each experiment the silver-treated plants were protected against infection. The degree of control was comparable to that given by bordeaux mixture, which was employed in these and all subsequent experiments as a standard comparative spray.

Two of the silver-soap mixtures and silver-lauryl sulfate were similarly tested on the same plant species inoculated with the same pathogens. Here again the silver sprays markedly reduced infection, with silver-lauryl sulfate possibly being the most effective.

The silver content of 100 p.p.m. has been arbitrarily chosen as the quantity which would permit of general application of silver compounds as sprays. Greater concentrations undoubtedly could be used for certain crops of high economic value. It was of interest, therefore, to study the degree to which the silver could be reduced below 100 p.p.m. and still inhibit germination of spores and control infection. A stock silver-lauryl sulfate suspension was prepared containing 50 p.p.m. of silver and a sodium lauryl sulfate concentration of 1:600. The stock suspension was progressively diluted to a silver content of 6.25 p.p.m., and each dilution was tested on excised potato leaves for its toxicity to the spores of *Alternaria solani*. From several experiments it was found that the minimum quantity of silver which completely inhibited spore germination of this fungus is 12.5 p.p.m.

A similar dilution series of silver-lauryl sulfate was tested for its ability to protect potato and carnation plants against infection by *Phytophthora infestans* and *Alternaria dianthi*, respectively, under greenhouse conditions. The suspension having 12.5 p.p.m. of silver was as effective as bordeaux mixture in protecting the potato plants against infection by *P. infestans*, and silver in quantities of 100 and 50 p.p.m. gave similar control of *A. dianthi* infection on carnations. In a subsequent greenhouse experiment *Alternaria* infection of carnations was again controlled by each of three silver sprays containing 100 and 50 p.p.m. of silver. From these several experiments it is evident that the minimum silver concentration necessary to control a disease will vary according to the sensitivity of the specific pathogen to silver. The silver concentration of 100 p.p.m. may be more than enough to control some pathogens, yet insufficient for others.

Several of the silver compounds have been tested under field conditions for the control of various diseases. The performances of the silver sprays in those experiments where disease developed have been exceedingly variable. During the summer of 1938, the silver-lauryl sulfate spray satisfactorily controlled late blight of celery, whereas

silver oxide and colloidal silver gave only moderate protection. During the summer of 1939 silver-lauryl sulfate, silver dichromate and silver oxide reduced apple scab infection of leaves and fruits to approximately one-third to one-half that found on the unsprayed controls. Silver-lauryl sulfate and silver chloride were entirely unsatisfactory for controlling late blight infections on potatoes. This field performance of several sprays tested is very similar to that reported in the literature for the earlier tested silver-soap mixtures.

A series of laboratory and greenhouse experiments was conducted to determine, if possible, the reason for this poor protection by the silver sprays under field conditions. Since adhesiveness is a primary requisite for successful field sprays, this property of several of the field-tested materials was investigated. The laboratory method consisted of spraying known quantities of each silver spray on paired sets of glass slides. One set of slides was exposed to constant washing in distilled water for 20 minutes at 25 °C. Spores of *Alternaria solani* were then placed on both sets of slides to germinate. By this method the relative adhesiveness of a number of sprays was determined. The greenhouse adhesiveness experiments consisted of spraying separate lots of potted potato plants with each silver spray. Some of the plants from each lot were subjected to an artificial rain treatment. Inoculation with *Phytophthora infestans* demonstrated the relative adhesiveness of the several sprays tested. The adhesiveness of the silver-soap mixtures and the simple inorganic silver compounds was found, by both methods, to be very poor in comparison with bordeaux mixture. The failure to obtain protection with those silver sprays tested in the field during 1938 and 1939 was due, at least in part, to their poor adhesiveness.

Table 2.—Adhesiveness of Silver Sprays to Potato Foliage

Spray Material	Mean number of lesions per leaf from 6-9 replicate leaves	
	No rain	Artificial rain
Control	21.0	15.4
Silver oxide in bentonite	0.8	17.1
Silver sulfate in bentonite	0.04	8.2
Reduced silver in bentonite	0.7	11.8
Silver cyanide	0.04	11.1*
Silver-lauryl sulfate	0.0	7.3
Silver+manganous sulfate+hydrated lime	0.5	0.6
Silver+ferric sulfate+hydrated lime	0.05	0.09
4-4-50 bordeaux mixture	0.0	0.0

\*Received 5.2 inches of rain.

One of the major problems in developing a protective silver fungicide is to increase the adhesiveness of silver and at the same time retain its superior toxicity. From the discussion based on the literature in the preceding section of this chapter one may reasonably question the advis-

ability of using proteinaceous materials as possible adjuvants to increase the adhesiveness of silver, because such materials apparently reduce the toxicity of the silver ion to fungi. The writers have tested a few inorganic compounds which, when added to the silver, might possibly increase its adhesiveness. Silver salts have been precipitated and silver nitrate chemically reduced in a 0.5 per cent bentonite suspension. Solutions of silver sulfate have been separately admixed with several metal sulfate solutions, and the resulting mixture precipitated with a calcium hydroxide suspension. In Table 2 are presented data from a number of greenhouse experiments in which the adhesiveness of silver sprays to potato foliage was tested. In all cases the silver content was 100 p.p.m. The manganous sulfate, ferric sulfate, and hydrated lime concentrations are 0.6, 0.8 and 1.0 per cent, respectively. The sprayed plants given the artificial rain treatment received a total of 7.3 inches. Approximately one-half of this rain was applied on each of two successive days. All plants were inoculated with the swarm spores of *Phytophthora infestans*.

These data are not strictly comparable as they were taken from a number of separate experiments, but they clearly indicate the type of data which have been obtained from the studies on adhesiveness. Silver-lauryl sulfate, when tested under field conditions, gave unsatisfactory protection to the sprayed plants in certain cases. From the data in the table above it is clear that silver-lauryl sulfate and silver cyanide adhere very poorly to potato foliage. The failure of bentonite to increase the adhesiveness is also demonstrated by these data. The adherence of silver spray mixtures containing manganese and iron is particularly encouraging in that they demonstrate the possibility of producing a silver spray in which adhesiveness will not be a limiting factor under field conditions. The iron and manganese at the concentrations used apparently have no toxic action on *P. infestans* as shown by other experiments.

A large number of other possible silver mixtures remain to be similarly tested. Many of them will be discarded because of poor adhesiveness, while some will be sufficiently promising to warrant further testing. Any mixture so discovered must be subjected to varied field conditions before its true value as a protectant can be evaluated.

The silver sprays thus far studied have possessed several properties which should make them desirable in practical use. Owing to the great dilution of silver, the visible residue left on the sprayed foliage is negligible, except in the case of silver-manganese and silver-iron mixtures. In these cases the visible residue can be minimized by reducing the quantity of manganous and ferric sulfate employed in their preparation. The suspensibility of the various silver materials in water has been satisfactory in many cases. Ease of preparation and of application have presented no special difficulties. The possession of these essential properties by any future silver spray will have to be determined.

The relative cost of silver sprays in comparison with other spray materials has frequently been raised as the major obstacle in producing

a practical silver fungicide. The cost of silver nitrate per pound is of the order of one hundred times that of cupric sulfate pentahydrate. For this reason the writers have arbitrarily chosen 100 p.p.m. as the silver concentration with which to experiment. If we assume the cost of silver nitrate to be six to seven dollars per pound, it would cost from 79 to 92 cents per 100 gallons of spray for the silver at this concentration. The final cost of a silver spray will depend upon what adjuvants must be added to produce a satisfactory spray. If these materials are inexpensive, the cost per gallon may be of the order of magnitude of 1 cent, which is not an excessive cost for the spraying of many crops.

#### SILVER AS A SEED DISINFESTANT AND DISINFECTANT

It is a common practice to treat seed with chemicals to destroy surface-borne saprophytes and pathogens which are adhering to the seed. This process is usually discussed as seed disinfection. The writers believe this term has been loosely applied in many cases and in the following discussion have chosen to restrict its meaning. Seed disinfection, as here employed, means the destruction of organisms which have already established a vital relationship with the living structures of the seed. The destruction of organisms which are only in physical contact with the seed surface or which have invaded only the non-living cells of the seed coat tissues will be called seed disinfestation. A very few chemicals have been successfully employed as seed disinfectants, because of the difficulty of destroying the pathogen without injuring the embryo of the seed, but a great many chemical compounds have been effectively used for seed disinfestation.

Seeds are usually treated by dipping for two reasons: to eliminate contaminating surface organisms from seeds or other organs which are to be used for obtaining contaminant-free plants in experimental work or for the isolation of organisms, and to eliminate specific plant pathogens from seeds which are later planted for crop production. Silver solutions have been employed for both purposes.

Davies<sup>32</sup> found silver nitrate better than mercuric chloride for surface disinfestation in the isolation of *Ophiobolus graminis* from diseased tissue. After comparing a number of chemicals for disinfesting wheat seeds and roots, Mead<sup>33</sup> concludes that the silver nitrate dip is of no value when isolating organisms embedded in the tissues, because of its thorough action. He suggests that the treatment would be satisfactory for obtaining pathogen-free seedlings from diseased seed. Should the silver nitrate penetrate beyond the seed coat to any appreciable extent it might destroy the plant embryo. Thus, Schroeder<sup>34</sup> has found that the embryos of wheat and barley seed with broken seed coats are destroyed by the silver treatment. The same is true of pea seed, the seed coat of which is evidently permeable to silver nitrate. Shull<sup>35</sup> also has reported that the seed coat of *Xanthium glabratum* is permeable to silver nitrate.

Both Shull and Schroeder exposed the seed for periods of 12 to 14 hours up to several days. Shorter periods of treatment undoubtedly would limit the extent of silver penetration and consequent injury in seeds having permeable seed coats. All seed coats, however, are not permeable to silver nitrate. Schroeder<sup>34</sup> found that barley and wheat seed with sound seed coats are not injured by dip treatments of 24 hours in a 5 per cent silver nitrate solution, and that the toxic action is confined to surface-borne organisms. That the seed coats of barley (*Hordeum vulgare* var. *caerulescens*) are not permeable to silver nitrate has been confirmed by Brown.<sup>36</sup> From these observations it appears that the successful isolation of a pathogen from a plant organ disinfested with silver nitrate will depend, among other things, upon the conditions, the permeability of the plant tissue to the silver solution and the duration of the treatment.

Various workers<sup>4, 5, 33, 34, 37, 38</sup> have found that, for the elimination of spores of saprophytes adhering to seed surfaces, the silver nitrate dip is superior to other treatments. The writers have observed that 0.0092 molar silver nitrate solution is more effective in destroying the spores of saprophytic fungi adhering to wheat seed than is a .048 molar cupric sulfate solution. Certain organisms are evidently more resistant to silver than others. Pringsheim<sup>5</sup> found that of the few organisms which survived the silver nitrate treatment, spore-forming bacteria are the most common; Mead<sup>33</sup> found *Fusaria* and *Fusarium*-like fungi to be the most frequent survivors in his studies.

Silver solutions and mixtures have been tested and recommended as seed dips for the control of a number of surface-borne pathogens. Probably the most extensive work demonstrating the efficacy of silver solutions as seed disinfestants has been done with tobacco seed. Johnson and Murwin<sup>4, 39</sup> found that silver nitrate solutions are advantageous not only because of their marked toxicity to *Bacterium tabacum*, but also because of the slight reduction in seed germination resulting from the treatment. The silver nitrate dip has also been found effective in controlling other surface-borne bacterial pathogens of tobacco.<sup>40, 41, 42</sup> Seed treatment with silver nitrate likewise prevents seed transmission of the casual organisms in Alternariosis of tobacco,<sup>43</sup> tobacco black shank,<sup>44</sup> and tobacco frog-eye.<sup>45</sup> The apparent success in controlling seed-borne bacterial pathogens of tobacco by the silver nitrate dip has led to its general use in many tobacco-growing areas.<sup>41</sup>

Silver solutions have similarly been tested for the control of some surface-borne pathogens of wheat. Solutions of a proprietary preparation containing silver cyanide were found to be toxic to the chlamydospores of *Tilletia tritici*, destroying them when sprinkled on infested wheat seed.<sup>46</sup> The same material completely prevents infection by *Tilletia tritici* when the seed is dipped in solutions of various concentrations.<sup>47</sup> Since the spores of this pathogen are borne entirely on the seed surface it is possible for the toxic silver solution to come into intimate contact

with the spores. Christensen,<sup>48</sup> on the other hand, was unable to control infection by *Helminthosporium sativum* in wheat seedlings developed on sterile sand from infected seed previously dipped in a silver nitrate solution. His treatment likewise failed to control secondary root-rot and stem-rot under field conditions. According to Christensen,<sup>49</sup> *Helminthosporium sativum* is apparently carried over from season to season as vegetative mycelium within the seed. It also infests the soil. When seeds are infected, it is doubtful that the silver nitrate will be effective in destroying the pathogen, as was pointed out earlier. As will be shown later, seed treatment with silver nitrate solutions is not effective as a protectant against damping-off fungi which infest the soil.

Silver solutions have been found to destroy the bulb nematode and bulb fly larvae of narcissus.<sup>51</sup> When the silver ion is combined in the complex silver-cyanide anion the silver is less readily removed from solution by the bulbs and adhering soil and seems to be as toxic as the silver ion alone. This appears to be a promising approach in using silver as a seed, bulb or tuber disinfectant, particularly where the same solution is to be repeatedly used for treating several lots.

The writers have carried out a number of experiments with silver nitrate solutions as seed and tuber disinfectants and protectants. For the disinfection experiments, potato tubers bearing viable sclerotia of *Botryobasidium solani* (*Rhizoctonia solani*) were dipped according to the hot and cold procedures commonly followed when treating tubers with mercuric chloride.<sup>50</sup> Infested tubers were dipped in hot and in cold solutions, each containing the same amount of mercury and silver, i.e., 750 p.p.m. The sclerotia were aseptically removed and planted on sterile potato-dextrose agar; the treated sclerotia failed to grow in every case, whereas all those untreated grew.

Experiments were then conducted to determine the minimum silver concentration necessary to kill all the sclerotia. Infested tubers were given the cold treatment (30 °C for 1½ hours) in a series of silver nitrate solutions with silver concentrations varying between 500 and 100 p.p.m. It was observed that the killing efficiency of a given silver solution depended, in part, on the size of the sclerotia. The larger sclerotia were those which survived. From the data obtained in these experiments the effective minimum silver concentration in the dip solution is probably of the magnitude of 250 p.p.m. or greater.

When a mercuric chloride solution is used for treating potato tubers it is occasionally necessary to replenish the mercury adsorbed by the tubers, adhering soil and container.<sup>50</sup> The silver nitrate concentration is likewise diminished when several lots of narcissus bulbs are dipped in the same solution.<sup>51</sup> An experiment was therefore carried out in glass beakers to obtain information as to the extent to which silver is adsorbed from solution by the potato tubers. Samples of infested tubers were washed free of adhering soil and dipped successively for 1½ hours at 27 °C in 400 cc of a silver nitrate solution which contained, at the begin-

ning, approximately 1 mg of silver per cubic centimeter. After each sample of tubers was treated, an aliquot of the solution was analyzed potentiometrically with potassium iodide as the titration solution, to determine the amount of silver removed by the tubers. Sclerotia from each set of treated tubers were aseptically removed and tested for their viability. The data from this experiment are given in Table 3.

Table 3.—Adsorption of silver from a Silver Nitrate Solution in which successive lots of Potato Tubers were dipped.

ato Sample No.	Weight of potato sample (gms)	Number of tubers	Mg of silver per cc	Mg silver removed by tubers	Mg silver removed per tuber	% sclerotia viable
Check			0			60
1	291.5	3	0.992	.043	.0143	0
2	291.0	3	0.949	.034	.0113	0
3	295.0	4	0.915	.050	.0125	0
4	293.7	3	0.865	.035	.0116	0
5	293.5	3	0.830			0

From these data it is evident that the silver cation is removed from solution by the materials being dipped, at a more or less constant rate. Had the adhering soil been left on the potatoes, the rate at which the silver was removed from solution would certainly have been greater, as has been pointed out by Newton *et al.*<sup>51</sup> The silver cation is readily taken up by many adsorbants and is chemically reduced or chemically combined with many organic and inorganic materials.

In a second series of experiments snapdragon and cucumber seeds were dipped in silver nitrate solutions containing 1000 and 100 p.p.m. of silver. The treated seeds were planted in soil heavily infested with damping-off fungi to see if the seed and the young seedlings would be protected from infection by these organisms. In most cases there was no evidence of protective action, or if there was, it was very slight in comparison with that given by the standard red cuprous oxide dust<sup>52</sup> employed as a check treatment. From these experiments it seems evident that the seed dip treatment with silver nitrate solutions is of no value as protection against pathogenic fungi which infest the soil.

After considering the literature cited above and the authors' experimental data, it is evident that silver can be successfully employed to disinfest seed of adhering saprophytes and pathogens. The resistance of some bacterial and fungal forms to the toxic action of compounds of silver may limit its use in many cases. Its utility as a seed disinfectant and as a seed dip treatment for controlling diseases caused by pathogens which commonly infest the soil is of doubtful value. The removal of silver from solution by the dipped seeds or other plant organs becomes an important problem when dipping succeeding samples in the same silver solution. Combining silver in a complex ion, as was done by Newton *et al.*,<sup>51</sup> seems to be an encouraging approach for the solution of this problem. The extent to which silver may be employed for seed disin-



festation is dependent upon further research and the relative cost in comparison with other materials.

#### SILVER AS A SOIL DISINFESTANT

Various chemical solutions have been injected into or thoroughly mixed with soil to free it of pathogenic organisms. Most of the chemicals used for this purpose have a high vapor pressure at ordinary temperatures and their toxic vapors permeate through the infested soil, destroying the undesirable organisms. The vapor pressure of inorganic silver compounds at ordinary temperatures is negligible, and these compounds do not permeate through the soil as a gas when introduced into it. Owing to their marked toxicity toward fungi and bacteria it has been suggested that dilute silver solutions might be used as irrigation water to destroy the damping-off fungi (*Rhizoctonia* spp. *Pythium* spp., etc.) commonly indigenous in greenhouse and cold-frame soils. These fungi are a serious problem in the production of many kinds of seedlings.

Since no experimental data are available on the problem, the writers conducted a number of experiments to test the soil disinfecting action of silver solutions. Untreated seeds were planted in flats containing greenhouse soil infested with damping-off fungi. Some of the flats were watered from the beginning with silver nitrate solutions containing 1000 and 100 p.p.m. of silver, and tap water was applied to the control flats. Two or three applications were made between the time of planting and the time when the seedlings were counted. These treatments were found to be toxic to young tomato seedlings. A single treatment with each of these silver solutions was therefore made immediately after planting on different flats sown with cucumber seed. Subsequent waterings were made with tap water. In this experiment the more concentrated solution was very toxic. In all subsequent experiments silver concentrations of 100 and 10 p.p.m. were employed. A single application only was made with the more concentrated solution (100 p.p.m.) immediately after planting. The more dilute silver solution was applied at regular intervals. The red cuprous oxide dust was used as a check treatment.<sup>52</sup>

In a series of experiments with cucumber and snapdragon seeds, neither of these silver solutions protected the seed or seedlings against the damping-off fungi. In fact they may have intensified the action of the fungi by a predisposition or weakening of the plants. That the silver did not eliminate the fungi from the soil was evidenced in a number of cases where seedlings emerged from the silver-treated soil and were later destroyed by the damping-off fungi.

It was suspected, in the above experiments, that the weaker silver solutions might be reducing the germination of the seed and subsequent seedling development. This, however, was disproved by first disinfecting the soil with formaldehyde<sup>53</sup> and then watering planted seed of gypsophila, snapdragon and cucumber with silver nitrate solutions

varying in silver concentration from 1 to 20 p.p.m. The seedlings which developed in this experiment were in all visible aspects no different from those in flats to which only water had been applied, except in one flat of snapdragon seedlings watered with the 20 p.p.m. silver solution. These seedlings were slightly dwarfed. This species had previously shown sensitivity to this concentration of silver.

The work of Jensen<sup>54</sup> suggested that the silver is adsorbed or chemically combined by the soil particles and made inactive. The more concentrated solutions, 1000 and 100 p.p.m. caused the soil surface to darken because of the formation of light-sensitive compounds. Algae which commonly grow on the surface of greenhouse soils failed to develop on the surface of the silver-treated flats, indicating that the silver was still in a toxic form or had destroyed these organisms when first applied to the soil. When the 1000 p.p.m. silver solution was applied after planting only, and before the seeds had started to germinate, the seedlings which later developed were killed either before they emerged from the soil or during the process of emergence. This seedling injury further indicates that the silver is still in a form toxic to plants even after several days' contact with the soil. It is possible that the fungous bodies in or near the soil surface were destroyed and that actual infection was caused by the deeper-living organisms. It is evident from these studies that silver nitrate solutions applied as irrigation water for the destruction of soil infesting damping-off fungi are impractical.

This lack of soil disinfecting action by silver compounds is apparently not true for species of the soil micro-fauna. Hovy<sup>55</sup> has briefly reported that silver proteinate mixed with fertilizer and applied at the rate of .3 gram per plant gave perfect control of tobacco eelworm (*Heterodera marioni*). This rate of application is equivalent to three metric pounds per acre. No other data pertaining to the control by the use of silver of plant pests which infest the soil have been found in the literature.

#### MISCELLANEA

The injection of medicinal substances into the animal body to cure various diseases frequently suggests an analogous treatment for the control or cure of plant diseases. In no case has the injection of medicaments into a plant body met with the success that has accompanied such practices in animal pathology. Attempts have been made to control various vascular diseases of plants by injecting chemicals into the vascular systems.

The writers injected suspensions of silver oxide and silver chloride into the stems of tomato plants. Some of the more soluble salts, when so injected, killed the tomato plants. The silver oxide likewise killed the younger plants. The older plants which survived the injection were inoculated four weeks later with *Phytophthora michiganensis*. The injected plants became infected as readily as the control plants. Solutions of certain inorganic silver salts introduced into the vascular systems of elm

trees \* are toxic to the trees. The adsorption of the silver cation by organic materials would probably be a major difficulty with silver solutions sufficiently dilute to be harmless to the plant.

Fungicidal dusts are used extensively for the control of many plant diseases. The possibility of using silver in such a capacity has never been investigated. In other connections various inert materials have been impregnated with metallic silver and given germicidal properties.<sup>64, 65</sup> Dustable inert materials may likewise be activated with metallic silver or silver compounds and may be of practical value as fungicidal dusts.

The treatment of freshly exposed tree wounds caused by accident, pruning, etc., are frequently washed, dipped or painted with fungicidal or bactericidal preparations to prevent entrance of pathogenic organisms. The fungicidal activity of silver suggests a possible practical application for these localized treatments.

The extent to which silver may be used as a fungicide in any of the capacities discussed in this chapter will be determined in future research. The toxicity of various elements to pathogenic organisms is the basic property which has led to the development of our present practical fungicides. Since this property is so markedly possessed by silver, one can reasonably expect that a practical fungicide will be developed with silver as the toxic constituent.

\* Unpublished data of Dutch Elm Disease Investigations conducted by New York State College of Agriculture at Boyce Thompson Institute, Yonkers, N. Y.

# Chapter 18

## Miscellaneous

By LAWRENCE ADDICKS

### SILVERWARE

Modern American silverware—forks, spoons, bowls, etc.—is either of “sterling” composition (92.5 per cent silver and 7.5 per cent copper) or “plated” with a very thin fine silver coating on base metal. The production of such ware forms an industry of long standing and the Silver Project has had no contact with it beyond studying the electroplating technique employed and the tarnish resistance of any silver-rich alloys produced in the course of the metallurgical studies.

Sterling composition, while established empirically, has never been improved upon and would survive regardless of the value imparted by the long-used stamp of quality. It is, however, subject to rapid tarnish in the presence of sulfur or its compounds, even more so than fine silver, due to the copper component, and it has long been argued that tarnish-free sterling would command a greatly enlarged market. The problem is difficult because the silver content must be at least 92.5 per cent in order to warrant sterling classification, the color of the surface must be that of clean sterling, and the workability for spinning, etc., must remain unimpaired. To date, this problem has not been satisfactorily solved from the silversmith's point of view.

Plated ware, while perfectly satisfactory for table use, is not of adequate thickness nor sufficiently free from pores to have entered technical use. It has not been found possible to purchase thin pore-free plate at any commercial establishment that has been investigated. This has doubtless been the reason why many technical applications were not further developed long ago.

The statistics of consumption are discussed in the next chapter. It will be noted there that the market appears to be saturated, and that additional consumption is likely to come only from a solution of the tarnish problem, or from such a fall in price as will shift the plated-ware demand over into the sterling field, where the metal value is the chief cost factor.

### COINAGE

Coinage has not been considered as an industrial use because “hard money” is no longer in demand as legal tender, and today subsidiary coins have become merely tokens, so that there is no very good reason for

using silver in their composition. At this writing an American quarter-dollar has a silver content value of but a little over six cents; in countries with debased coinage, such as Great Britain, the discrepancy is much larger. It is therefore a declining use with no remedy evident.

### SILVER SALTS

The nitrate is the starting point in the manufacture of silver salts. The conversion of commercial silver bars into a highly purified silver nitrate is a very simple operation. From this salt are prepared the photosensitive halides used in photography, the cyanides used in electroplating, and most of the minor salts.

In examining the technical and pharmaceutical uses of silver, the only opportunity for productive investigation that suggested itself lay with the sulfide. To begin with, this salt has a nuisance rating as a tarnish\* and the more known about it the better; then it has some rather unusual properties. Indirectly the oxide called for some attention on account of the "spitting" of molten silver and the behavior of silver diaphragms. So these two salts were given some attention.

*Silver sulfide* is the grayish-black tarnish which forms in contaminated atmospheres on silver and which is wholly free from oxide and chemically quite inert. It has negligible uses in making glass ray filters, in niello inlays and "oxidized" finishes on silverware.

As long ago as 1861 Percy described (J2-161) the production of "moss" silver by the reduction of the sulfide and Beutell (Q-1) is quoted by Mellor (J2-162) as follows:

When natural or artificial silver sulfide is heated in an evacuated sealed tube for several days at a temperature of 350° to 600° a certain amount of decomposition takes place. The small amount of silver formed seems to wander through the silver sulfide, appearing at the cooler end of the tube in the form of hair silver. A number of experiments which were made showed that neither silver foil nor hair silver is attacked by sulfur vapor in a vacuum at 350°; the metal remained bright after forty-eight hours. Silver foil heated alone in a vacuum for a long period at 450° to 585° showed no trace of the growth of hair silver, but when silver foil and silver sulfide were heated together at 450° remarkable growths were obtained in a comparatively short time. To obtain these growths it was necessary for the silver and the silver sulfide to be actually in contact.

This description is interesting in connection with the little understood function of traces of sulfur compounds in photographic emulsions.

In 1917 work was done on silver sulfide by Vinal (J2-159) at the Bureau of Standards, who summarized his results as follows:

Silver sulfide may be prepared in the form of short wires or thin strips like a metal. The wire, which must be drawn hot, has been

\* See Chapters 12, 15, and under *Silverware* in Chapter 18.

found to conduct electricity like a metal of high specific resistance and practically zero temperature coefficient. The strip of sulfide, rolled at room temperature, has a large temperature coefficient and shows both metallic and electrolytic temperature conduction at the same time. It has a volt-ampere curve characteristic of a pyroelectric conductor. The resistance of these strips has been examined with both alternating and direct current, with the result that the alternating current resistance was nearly always found to be higher than with the direct current and the passage of a small alternating current of a frequency as low as 60 cycles increased temporarily the resistance of the sulfide, while a small direct current produced the opposite effect.

The Lehigh fellowship of the Silver Research Project (J1-164) examined these relations with particular reference to the supposed plastic properties of the sulfide. The following paragraphs are abstracted from the reports of this work.

When silver sulfide is heated in a muffle and the temperature held at 400 °C, it is partly changed to metallic silver which is formed in curled threads growing from the body of the mass. Upon raising the temperature to 600 °C all of the sulfide is converted to moss silver, which remains unchanged, beyond some sticking together of the filaments when the temperature is raised nearly to the melting point. These threads are catalytically active without further treatment.

Inasmuch as a conducting plastic would find immediate application in the preparation of electrotypes, the ability to take impressions was used as a measure of the plasticity of silver sulfide. The fused salt was found to be too hard to take impressions when cold, and when heated, although it was workable, there was some reduction to metallic silver. Discs were then made by the consolidation of the powdered sulfide at pressures up to 33,800 l.p.s.i. and at temperatures from 20 °C to 300 °C. Up to 5600 l.p.s.i. these discs were brittle and frangible, while at higher pressures there was formed a hard solid mass which could be cut with a knife like lead, and could be hammered and rolled with difficulty, although it had a tendency to crack at the edges. Good impressions of a coin were obtained using discs  $\frac{3}{8}$ " thick and pressures ranging from 12,700 to 15,000 l.p.s.i. Such pressures are quite beyond the defacement resistance of typemetal.

*Silver oxide* was next examined. No actual laboratory work was conducted beyond heating the powdered oxide in the air, when it first changed from black to white and then to moss or sponge silver as in the case of the sulfide, but more massive in type. Some theoretical consideration, however, was given to the idea of utilizing the property molten silver has of dissolving some 20 volumes of oxygen, nearly all of which it rejects upon freezing, as the basis of cyclic extraction of oxygen from the air. A second approach to the same goal would be to "filter" air, through a silver diaphragm which will pass oxygen by diffusion, thereby impoverishing the air on one side of the diaphragm and enriching it on

the other at a rate per unit of surface depending upon the temperature and pressure gradients (J1-164).

Oxygen-enriched air has great possibilities in increasing the smelting capacity of blast furnaces. It has also been suggested that air moderately impoverished in oxygen might give a breatheable atmosphere in which coal dust would not detonate. While purely speculative, it seems worth while to conclude this section by reproducing below the report by Butts and Van Duzee (J1-164):

### Solubility of Oxygen in Silver

It is known that silver will dissolve about 20 times its own volume of oxygen near the melting point. Calculations were made to determine whether this behavior might be taken advantage of in the enrichment of furnace blast. The process might use either a temperature cycle or a pressure cycle.

The following figures show the possibilities of a temperature cycle with a 50° drop in temperature.

Oxygen occluded at 973 °C	21.35 vol.
Oxygen occluded at 923 °C	.56 vol.
Oxygen obtainable from 50 °C drop	20.75 vol.

From this it can be seen that for every 20.75 cubic feet of oxygen, 1 cubic foot of silver would be necessary. Using the same example for enrichment as in the case of diffusion in Table 1, 36.14 cubic feet of silver would be required for a 1 per cent enrichment of the blast. This assumes that the cycle would be completed in one minute. Although data are not available which will permit the calculation of the rate of solubility, it is known that the maximum solubility is obtained only after several minutes. Thus, it is quite probable that one heating-cooling cycle per minute could not be realized. However, the absorption curve is very steep during the first minute and perhaps at high temperature the absorption is nearly complete in that time. Data concerning the rate of solubility at high temperature are not available nor has anything been done on the application of such a process to air enrichment even on a laboratory scale.

The use of a pressure cycle, absorbing oxygen from air at one pressure and releasing it at another, has been suggested. It is known that the rate of solubility increases directly as the square root of the pressure. The pressure curve would be less steep than a curve for temperature changes and the pressure change would necessarily be great. It must be remembered that in pressure changes we would be dealing with total pressure of the atmosphere, of which only one-fifth is the partial pressure of the oxygen.

It is possible that a combined pressure-temperature cycle might be used. However, with the available data, it is not possible to calculate

the possibilities of such a cycle. Little thought has been given to the mechanical arrangement for a process involving pressure changes.

Conference with engineers of a large steel company has confirmed their interest in the possibilities of blast enrichment, at present dormant because of the very high cost of any known method. Recent experimental blast furnace work in Germany indicates increase in furnace capacity of several per cent and/or saving of several per cent of coke with blast enrichment of 3 per cent or less. Since the annual production of a 1200-ton iron furnace would have a market value of over \$8,000,000 at present prices, a large investment could profitably be made in blast enrichment if a satisfactory method could be found.

### Diffusion of Oxygen through Silver

The study of oxygen diffusion through silver has been purely theoretical, no experimental work having been advisable up to this point because of the considerable time required to build the necessary apparatus, and because significant experimental data were found in recent literature (J1-164). The figures obtained are based upon certain temperature and pressure conditions and thicknesses of silver foil. It is not known whether or not these factors could be coördinated to the desirable values in actual practice. The foil thickness must be such that it can, when properly supported, withstand fairly high pressures. Since the rate of diffusion varies inversely with the thickness of the foil, the foil must be as thin as possible to obtain the best results. Temperature is the most important factor in the rate of diffusion. Calculations have been made up to 800 °C. It is not known how well a very thin silver foil would withstand such a temperature under moderately high pressures. If, however, it were possible to increase this temperature even a few degrees, the rate of diffusion would be materially increased.

Pressure is less important in the rate of diffusion. A change of one or two atmospheres pressure has less effect on the rate of diffusion than relatively small changes in temperature or foil thickness.

Calculations were based on the following equation:\*

$$D = \frac{1.71}{10^{43}} \times \frac{\sqrt{P}}{d} \times T^{14.62}$$

in which  $D$  is the rate of diffusion in cc per square meter per hour,

$P$  is the pressure of the oxygen in millimeters,

$d$  is the thickness of the silver in millimeters, and

$T$  is the absolute temperature.

Two other equations were also studied:

$$D = \frac{43,054}{d} \times \sqrt{P} \times T \times e^{\frac{43,232}{4T}}$$

\* F. M. G. Johnson and P. Larose, *J. Am. Chem. Soc.*, **46** 1377 (1924).



and

$$D = \frac{K}{J} \times \sqrt{P} \times e^{-\frac{v}{2kT}}$$

in which  $E_0 = 45,200$

$$K = 0.0375 \text{ or } 0.0206$$

Calculations were made of the amount of silver necessary for enrichment of the air requirement of an iron blast furnace by one per cent (*i.e.*, from 21 to 22 per cent oxygen). Table 1 shows the amount for a furnace producing 1200 tons of iron per day.

Table 1.—Silver Required for Enrichment by Diffusion of the Blast of a 1200-Ton Iron Blast Furnace from 21 to 22 per Cent Oxygen

Diaphragm Thickness (mm)	Partial Oxygen Pressure (mm)	Temp. (°C)	Diffusion (cc/m <sup>2</sup> /min)	Area necessary for 1% enrichment (sq m)	Vol. necessary for 1% enrichment (cu m)	Weight of Ag (Troy oz)
.2	5(760)	800	179	118,600	23.7	8,000,000
.1	5(760)	800	358	59,300	5.9	2,000,000
.1	5(760)	700	85	249,800	24.98	8,433,000
.1	3(760)	800	277	76,600	7.66	2,585,800
.1	3(760)	700	66	321,000	32.1	10,836,000
.1	2(760)	800	225	94,390	9.44	3,196,000
.1	2(760)	700	54	393,000	39.3	13,267,000
.05	5(760)	800	717	29,600	1.5	500,000
.05	5(760)	700	171	124,100	6.2	2,341,000
.05	3(760)	800	554	38,335	1.91	644,000
.05	3(760)	700	132	160,800	8.04	2,714,000
.05	2(760)	800	451	47,195	2.36	796,000
.05	2(760)	700	108	196,600	9.8	3,298,000
.05	760	800	318	66,783	3.34	1,127,500
.05	760	700	75	283,100	14.15	4,777,000
.01	5(760)	800	3583	5,930	.059	19,900
.01	5(760)	700	856	24,800	.248	83,700
.01	4(760)	800	3180	6,600	.066	22,200
.01	4(760)	700	760	27,900	.279	94,000
.01	3(760)	800	2770	7,660	.076	25,600
.01	3(760)	700	660	32,000	.32	108,000
.01	2(760)	800	2250	9,400	.094	31,700
.01	2(760)	700	538	39,400	.394	133,000
.01	760	800	1590	13,350	.1335	45,000
.01	760	700	378	56,100	.561	189,300

## PHOTOGRAPHY

The field of photography has been so thoroughly studied in both its scientific and its commercial aspects that mention of it may be confined to its silver-consuming possibilities. Many chemical compounds are photosensitive, so that it is theoretically possible to make pictures without the use of silver and limited use is actually made of silver-free materials, as in the case of blueprints based on iron salts. There is nothing on the horizon at present, however, to indicate any displacement of the suspension of minute silver halide crystals in gelatin as a medium in all but highly specialized fields of minor importance.

There are three main divisions of the industry: motion picture studios, professional photographers and amateurs. Roughly, the net amount of silver used in the preparation of films and papers for all purposes totals at present around 10,000,000 ounces a year in the United States and perhaps 15,000,000 ounces in the world. Unfortunately for silver consumption, very high scrap recovery from discarded films and darkroom reagents is not technically difficult, the problem being largely one of collection of the waste materials. A substantial proportion of the film produced is exposed by amateurs and to date this has been discarded; but where sufficient quantity is involved in professional use recovery measures have been instituted, while it is reported that in Germany tank cars travel around systematically collecting foul hypo solutions. We therefore have to discount consumption perhaps 50 per cent in considering the absorption of silver.

### MEDICINE

While medicine cannot be classed as an industry, it is one of the minor fields in which silver is consumed. In one form or another silver is employed as a caustic, an astringent or an antiseptic in topical applications, and smaller amounts are administered intravenously and orally. Its marked bactericidal powers have been increasingly recognized in recent times and silver protein compounds have had wide application in the treatment of nose and throat ailments.

In view of the fact that there is no scrap return in the pharmaceutical field and silver has had no systematic study in its medical applications, it seemed worth while early in the Project's life to consider the desirability of some exploratory work. The so-called oligodynamic property of silver,\* whereby one part of ionized silver in over 100,000,000 parts of water has marked killing power on many pathogenic bacteria, seemed to have had scant recognition in America; consequently, a few simple experiments were undertaken to establish the validity of the claims. There are opportunities for the widespread application of this idea in the protection of the scattered small-scale water supplies of many rural districts, in air-conditioning where scrubbing and humidification apparatus must not become a breeding ground for bacteria and where no chemicals imparting odor can be used, in the control of bacterial conditions in wine and vinegar making, etc. Only a confusion created by foreign-owned patents coupled with the deranged financial situation in Europe have prevented vigorous exploitation of these fields.

The Project itself supported one short term fellowship in bacteriology, but it was soon realized that (1) the field was enormous; (2) medical research groups were too absorbed at the moment in the marvelous developments connected with sulfanilimid and its congeners to make it an appropriate time to introduce a new idea; (3) the work should be

\* See Chapter 16.

supported by those having a closer contact with medicine than a metallurgical group; (4) the problem really involved a review of the entire field of antiseptics and a lot of clinical work in cutaneous medicine. Reports from such medical men as we succeeded in interesting indicate that attempts to apply European experience in the use of silver as an antiseptic give unreliable results; that is, entire success will be achieved in one case and failure in another apparently similar one. This brings silver into the same category as the other antiseptic agents: iodine, chlorine, mercury, phenols, alcohols, dyes, etc.—all are effective only under suitable conditions. Silver has an advantage in its permanency, blandness, nontoxicity and selective action against the lowest orders of life. This should be taken up by a group interested in the fundamentals of the subject rather than merely in the promotion of silver, as there is today no universal antiseptic and the Rockefeller Foundation lists dermatology as one of the medical fields offering unique opportunity for research.

One field we did cover adequately—that of toxicology. The administration of silver, externally or internally, except in very large doses, results in no untoward systematic effects, but long-continued exposure creates a seldom seen but not actually rare condition known as argyria, the accumulation of silver in some form in the lower portion of the skin, and in other organs. This darkens from photochemical action and produces a pigmentation which is objectionable in appearance although it has no other ill effect. Inasmuch as no study of the records appears to have ever been made, a fellowship was established at the University of Pennsylvania Medical School resulting in the publication by Williams & Wilkins in 1939 of "Argyria, the Pharmacology of Silver" by Dr. William R. Hill and Dr. Donald M. Pillsbury, which contains a thorough and painstaking review of the whole subject, including a bibliography of over 600 titles.

At the present time medicine may account for 500,000 ounces a year, chiefly in the colloid protein suspensions.

#### STORAGE BATTERIES

A study \* of the effect of silver additions up to 0.15 per cent in antimonial lead storage battery grids has shown that as little as .05 per cent silver reduces the corrosion of alloys containing from 4 to 12 per cent antimony when corroded anodically in sulfuric acid of 1.285 specific gravity. Under the conditions of test, tensile strips containing from 0.1 to 0.15 per cent silver showed practically no loss in strength, whereas the controls lost from one-fourth to one-third of their strength under the same conditions. It was also shown that silver in the amounts mentioned does not promote self-discharge of the grids.

\* A. J. Dornblatt. Thesis, Effect of Silver on Some Properties and the Performance of Antimonial Lead Storage Battery Grids. Columbia Univ., 1940.

## DENTISTRY

BY IRL C. SCHOONOVER \*

Two types of alloys containing silver are of importance to the dentist: (1) the silver amalgams used as a restorative material for the filling of teeth, and (2) dental gold alloys containing silver from which metal appliances, inlays, etc., are prepared.

(1) *The silver amalgams* have been used as a restorative material for over a hundred years and were probably first used in 1826 as M. Taveau's "silver paste." They are unique in that the dentist has a plastic alloy which may be molded at mouth temperatures and which will solidify within a few minutes to a hard, brittle material capable of being polished. Furthermore, the change from the plastic state to the solid state occurs with but very little change in temperature.

An approximate idea of the physical properties of an amalgam can be gained from an inspection of some of the following requirements specified in the American Dental Association Specification No. 1 for Dental Amalgams.<sup>1</sup> This specification requires that an amalgam for dental use shall harden in 15 minutes after amalgamation, and that under a constant pressure of approximately 3550 pounds per square inch the amalgam will not flow more than 4 per cent in a period of 24 hours immediately following amalgamation.

Amalgams, which meet the above requirements have a compressive strength of between 20,000 and 50,000 pounds per square inch.

Dental amalgams may be considered as ternary alloys of silver, tin and mercury. Amalgam alloys from which amalgams are prepared are essentially silver-tin alloys to which small amounts of copper and zinc are added. An idea of the typical composition may be obtained from the specification referred to above. This specification requires that dental alloys shall contain not less than 65 per cent of silver, not more than 6 per cent of copper, not more than 2 per cent of zinc, and not less than 25 per cent of tin. The ideal composition is considered as that which corresponds to the formation of the compound  $\text{Ag}_3\text{Sn}$  in the silver-tin systems investigated by Rosenhain and his co-workers.<sup>2</sup>

Gayler<sup>3</sup> is of the opinion that the tin content in the amalgam alloy is the important factor and must not be less than 25 nor more than 26.8 per cent. Alloys have been prepared, however, in which the tin content varied between the limits of 20 and 35 per cent and the silver content between 50 and 75 per cent. It should be pointed out that these alloys low in silver have a tendency to shrink, flow, and have low compressive strength values.

Copper may be substituted for silver in amounts up to 6 per cent. The addition of copper not in excess of 6 per cent is thought to increase

\* Associate Chemist (former Silver Research Associate), National Bureau of Standards.

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Table 2.—Dental Materials. Chemical Composition of Casting Golds and Solders.

Alloy	Gold	Silver	Copper	Platinum	Nickel	Zinc	Iridium	Tin
1	71.3	7.1	9.9	10.62		0.08	0.14	0.83
2	78.0	10.0	5.9	6.1			.1	
3	71.4	6.0	15.6	2.78	1.98	2.38		
4	62.8	13.9	18.9		2.57	1.92		
5*	89.8	.04	10.0	.08				
6*	91.7	7.8	0.5					
7*	91.7	4.6	3.7					
8*	75.0	21.8	3.2					
9*	75.0	18.8	6.2					
10	65.4	15.4	12.4			3.9		3.1
11	66.1	12.4	16.4			3.4		2.0
12	65.0	16.3	13.1			3.9		1.7
13	72.9	12.1	10.0			3.0		2.0
14	80.9	8.1	6.8			2.1		2.0

\*Composition given is the batch formula.

the expansion during solidification, decrease the flow, and increase the strength of the amalgams.

The addition of zinc to dental amalgam alloys has been the subject of much controversy. Black,<sup>4</sup> in an investigation of amalgam alloys

Table 3.—Dental Materials. Physical Properties of Casting Golds and Solders.

Alloy	Heat Treatment	Tensile Properties				Brinell Hardness		Melting Range	
		Proportional limit (lbs. in. <sup>2</sup> )	Ultimate strength 3 inches (lbs. in. <sup>2</sup> )	Elongation in 3 inches (%) <sup>b</sup>	Modulus of Elasticity (lbs./in. <sup>2</sup> ) <sup>c</sup>	Tensile specimens	Dental Castings	°C	°F
1	Softened	50,000	64,500	1	13,000,000	154	150	910-1,010	1,665-1,850
	Hardened	61,000	84,000	—	13,000,000	195	196	910-1,010	1,665-1,850
2	Softened	22,500	48,000	18	11,000,000	90	82	940-1,025	1,725-1,875
	Hardened	26,500	50,500	14	12,000,000	98	94	940-1,025	1,725-1,875
3	Softened	53,500	69,000	4	13,000,000	145	143	885-985	1,620-1,805
	Hardened	94,500	108,500	—	14,000,000	249	222	885-985	1,620-1,805
4	Softened	46,000	70,000	10	13,000,000	149	148	820-870	1,510-1,600
	Hardened	73,000	103,000	1	13,000,000	214	202	820-870	1,510-1,600
5	—	17,500	48,000	31	11,000,000	76	—	925-940	1,700-1,725
6	—	3,000	21,500	25	—	32	—	1,050-1,050	1,885-1,920
7	—	11,000	34,500	20	—	54	52	970-1,020	1,775-1,875
8	—	11,000	36,000	19	11,000,000	56	—	925-995	1,700-1,825
9	—	18,000	45,500	18	12,000,000	74	—	895-980	1,650-1,795
10	Softened	27,000	42,500	14	11,000,000	111	—	745-785	1,375-1,445
	Hardened	55,000	63,000	1	12,000,000	185	—	745-785	1,375-1,445
11	Softened	29,500	44,500	12	11,000,000	103	—	750-805	1,385-1,480
	Hardened	77,500	83,500	—	12,000,000	193	—	750-805	1,385-1,480
12	Softened	30,000	44,000	9	12,000,000	111	—	765-800	1,410-1,470
	Hardened	77,000	92,000	—	13,000,000	199	—	765-800	1,410-1,470
13	Softened	24,000	36,000	7	11,000,000	103	—	755-835	1,390-1,535
	Hardened	61,500	70,000	—	12,000,000	180	—	755-835	1,390-1,535
14	—	20,500	37,500	18	11,000,000	78	—	745-870	1,375-1,545
24 karat	—	41,000	16,500	34	—	27	—	1,063	1,945

<sup>a</sup> Heat treatments designated by "softened" and "hardened" consist of quenching in water from 700 °C and cooling slowly from 450 °C, respectively. Those alloys for which no heat treatment is indicated were not appreciably affected by these treatments.

<sup>b</sup> Where no value for elongation is given, the value obtained was less than 1 per cent.

<sup>c</sup> Where modulus of elasticity is not given, this value was not determined.

<sup>d</sup> Less than 1,000.

containing zinc, observed an increase in the compressive strength and setting expansion of the amalgam. Gray<sup>5</sup> observed a slight continued expansion of dental amalgam alloys containing small amounts of zinc. Souder and Peters,<sup>6</sup> Ward and Scott,<sup>7</sup> and Taylor,<sup>8</sup> have investigated the effect on the physical properties produced by the addition of small amounts of zinc to the dental amalgams.

Factors other than the composition of the alloy which are known to affect the physical properties of amalgams are: aging of the alloy, particle size, method of amalgamation, pressure exerted on the amalgam during packing, and mercury content of the set amalgams. These factors have been studied in detail by Black,<sup>4</sup> Souder and Peters,<sup>6</sup> Gray,<sup>5</sup> Taylor,<sup>8</sup> Ward,<sup>7</sup> Gayler,<sup>3</sup> and Skinner.<sup>9</sup>

(2) *Dental gold alloys* containing silver are largely used for fabricating metallic restorations and appliances by casting. The silver in these alloys imparts a whitish color to the alloy, tends to raise the melting range of the alloy if it melts below the melting point of silver, and is said to contribute to its ductility. The metallurgy of these alloys is not too well known at the present time and little can be said as to how changes in the silver content of the dental gold alloys will affect their physical properties. The composition and physical properties of some typical dental gold alloys is given in Tables 2 and 3, based on data appearing in a paper by Coleman.<sup>10</sup>





## Chapter 19

### The Statistics of Industrial Consumption

By LAWRENCE ADDICKS

Anyone who sets himself the task of collecting and analyzing the available statistics covering the world's industrial use of silver will soon discover that it consists in an attempt to reconcile and piece together conflicting and fragmentary data. There are two main sources of information: Government agencies and the brokers and bullion dealers who have accumulated private knowledge of customer use, such as Handy & Harman of New York, Johnson, Matthey & Company of London and the Gold- und Silber-Scheideanstalt of Frankfurt-am-Main.

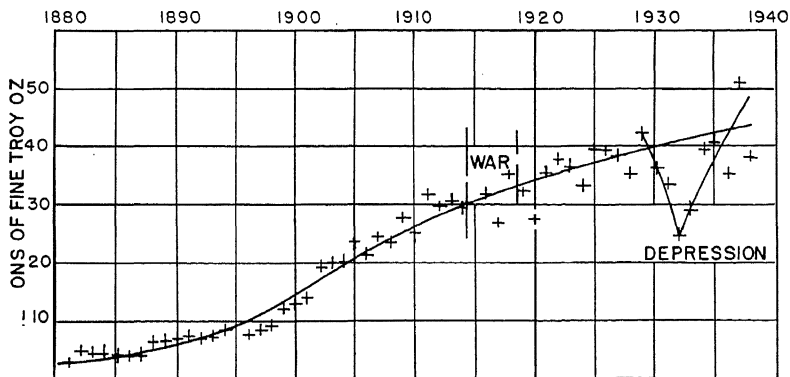


FIGURE 1. Annual gross industrial consumption of silver in the United States.

The United States Mint Bureau has painstakingly collected unclassified totals for the United States since 1880 by means of questionnaires sent annually to all known silver refiners and bullion dealers, every effort being made to avoid duplication due to the appearance of the same silver in different hands at various stages of its manufacturing life. These forms also call for separation of primary from secondary or scrap material. Some duplication undoubtedly exists; minor scrap cycles where small sweeps plants do a neighborhood business are naturally missed, and the melting of coins, negligible at the present bullion value of coin silver, has to be estimated. Nevertheless, these figures give a

fair perspective of the situation and they have therefore been plotted in Figures 1 and 2.

Figure 1 shows the total consumption for industrial purposes in the United States without any allowance for either mill scrap or old silver from previous years. Figure 2 shows the percentage of secondary material used, and over a term of years it doubtless presents an accurate trend, although subject to misconstruction for any individual year. In the early thirties, for example, there was a severe business depression when people needed cash, coinciding with a sharp temporary rise in the market price of silver, which resulted in drawing a disproportionate quantity of old silver out of hiding.

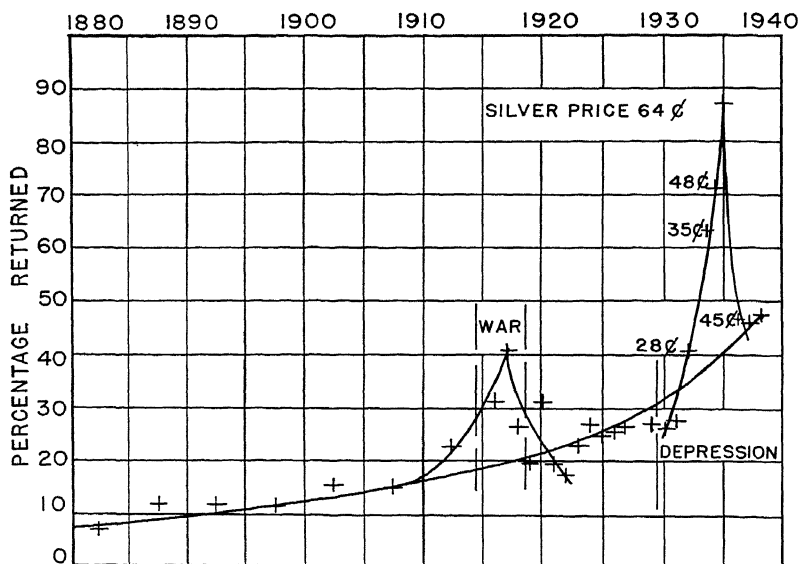


FIGURE 2. Scrap return of silver used industrially in the United States.

Since 1894 the Mint Bureau has endeavored through the activities of our diplomatic representatives abroad to compile similar tables covering the world. Here many additional difficulties are encountered. In the first place there are matters of definition involved. Industrial use has taken into account the "arts," and at times this term has been considered to include all Oriental imports not accounted for in monetary consumption, on the theory that the difference went into articles of personal adornment. This tangles industry up with hoarding. Then the schedule of countries reporting varies widely from year to year so that the grand total shows fluctuations which depend more upon

the number of returns than upon the world's consumption. Finally the troublesome question of scrap is handled arbitrarily in some periods and ignored in others. A careful review of all this material leads to the conclusion that no attempt to establish curves similar to those given for the United States is justified.

Taking into account figures from all sources and admitting a large factor of ignorance, the world consumption in industry for a representative recent year, without deduction for scrap and excluding Asia and Africa, might be assumed to be as follows:

Country	Fine Troy Ounces
United States	40,000,000
British Empire	12,000,000
Germany (present boundaries)	13,000,000
France	4,000,000
All others	6,000,000
Total	75,000,000

With scrap allowance, there is probably a net annual world consumption of about 50,000,000 ounces.

When we study the consumption of the United States we have two additional sources of data: the compilation made annually by Handy & Harman since 1919 and the independent survey made by the United

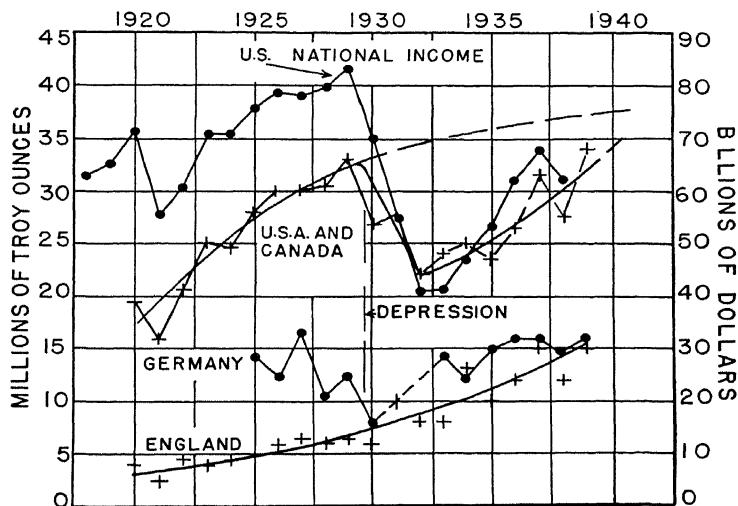


FIGURE 3. Net industrial consumption of silver (Handy and Harman).

States Bureau of Mines for 1928 to 1931 and published in two papers by Charles White Merrill (Economic Paper 14 and Information Circular 6647).

The Handy & Harman totals are plotted in Figure 3. It has been their custom to consider Canada jointly with the United States, so that the Canadian consumption of about 1,500,000 ounces must be deducted from each yearly figure when making comparisons. The estimates are based on manufacturing net requirements, that is, consumer goods produced after deducting mill scrap (such as perforated strip after spoons have been punched out) but without any consideration of whether the silver used is of primary or secondary origin. Since this system of scrap accounting did not completely cover all the minor industries until about 1931, they have kindly recalculated the earlier totals to make them strictly comparable throughout. As a matter of interest, the United States national income (as reported by the American Bureau of Metal Statistics) is also plotted, and a striking similarity will be noted to the total silver consumption. The dotted extension of the silver curve indicates the probable trend had business conditions been normal during the last ten years.

We have figures from all three sources for only four years. These are assembled in Table 1, Handy & Harman figures being adjusted for the exclusion of Canada.

Table 1.—U. S. Industrial Consumption in Millions of Troy Ounces

Year	Gross		Net		H & H
	Mint Bureau	Mines Bureau	Mint Bureau	Mines Bureau	
1928	35,500	37,200	24,900	25,800	29,000
1929	42,400	41,400	31,000	28,600	31,500
1930	36,300	35,100	26,900	24,000	25,500
1931	33,700	35,300	24,300	23,600	26,500
Ave.	37,000	37,300	26,800	25,500	28,100

These figures show fair correspondence. Theoretically the Mint total should be lower than the other two because it allows for consumer scrap as well as mill scrap. It would be reasonable to suppose that Handy & Harman with their special knowledge of the industry and long experience would cover the field more exhaustively than the Bureau of Mines as a temporary visitor. In any case the differences are not large enough to be significant.

In breaking down the total into specific uses we are virtually limited to the Bureau of Mines reports and the confidential figures of Handy & Harman, some of which they have kindly released for the purposes of this analysis. Of the years 1928-1931 covered by the Bureau, unfortunately only 1928 may be considered as typical. In 1929 America went on a spree and in 1930 and 1931 had a bad headache. For the record, however, there is reproduced in Table 2 the summary

of these years as drawn up in the Bureau circular, and we shall then examine the figures for 1928 more in detail.

Table 2.—U. S. Industrial Consumption in Fine Troy Ounces (Bureau of Mines)

	1928	1929	1930	1931
Sterling silver industry	9,429,922	9,871,644	7,548,803	8,823,593
	36.4%	34.4%	31.5%	37.4%
Photographic industry	6,560,812	7,616,741	7,546,451	6,587,623
	25.4%	26.6%	31.5%	27.9%
Electroplating industry	3,840,519	4,110,129	2,777,954	2,307,731
	14.9%	14.4%	11.6%	9.8%
Jewelry, optical goods and novelties industry	2,211,465	2,570,075	2,194,906	2,073,615
	8.6%	9.0%	9.2%	8.8%
Chemical industry (exclusive of photographic and electroplating)	1,537,890	1,753,863	1,685,701	1,461,548
	6.0%	6.2%	7.0%	6.2%
Industrials, including silver solder	1,699,399	1,974,908	1,153,615	1,224,820
	6.6%	6.9%	4.8%	5.2%
Dental supplies	501,802	598,322	611,369	649,984
	1.9%	2.1%	2.5%	2.8%
Miscellaneous consumption	5,950	80,855	384,223	358,547
	0.0%	0.3%	1.6%	1.5%
Total silver content of products	25,787,759	28,576,537	23,903,022	23,487,461
	99.8%	99.9%	99.7%	99.6%
Total losses (estimated)	38,795	24,774	78,142	91,494
Total silver consumption	25,826,554	28,601,311	23,981,164	23,578,955
	100.0%	100.0%	100.0%	100.0%
Scrap sent to smelters and refiners	11,412,129	12,824,952	11,138,356	11,673,701
Total silver turnover	37,238,683	41,426,263	35,119,520	35,252,656

In Table 3 the figures for 1928 are reassembled in more detail and with the scrap apportioned among the items.

The Handy & Harman figures for the three major industrial groups are plotted in Figure 4. Recent figures for the chemical industry have not been released, accurate totals being difficult to ascertain, owing principally to scattering purchases in the London market under present abnormal price conditions, but a compilation by the American Bureau of Metal Statistics shows *gross* consumption of silver for the production of nitrate as 12,500,000 ounces for 1937 and 11,900,000 for 1938.

In studying industrial consumption scrap return is a vital factor. There are five scrap cycles: The shortest is where a manufacturer takes used stamping strip, for example, and melts, casts and re-rolls new strip from it. This may be but a matter of days; it does not appear at all in yearly statistics and has largely disappeared now that the retreatment of scrap has become a well-developed business in its own right.

Table 3.—U. S. Industrial Silver Consumption in 1928 in Fine Troy Ounces

Industry	Purchases	% Scrap	Real Consumption	% Loss	Sales	% Total
<b>Silversmiths</b>						
Flatware					5,535,521	21.4
Holloware					2,689,827	10.5
Miscellaneous					1,204,574	4.7
Group Total	18,418,527	48.7	9,446,697	0.2	9,429,922	36.6
<b>Electroplating</b>						
Flatware					3,083,213	11.9
Holloware					551,356	2.1
Miscellaneous					205,950	0.8
Group Total	4,696,706	18.2	3,845,742	0.1	3,840,519	14.8
<b>Chemical (excl. electropl. salts)</b>						
Photography	7,910,605	16.9	6,575,939	0.2	6,560,812	25.4
Mirrors					325,346	1.4
Laboratory and Medicinal					235,676	0.9
Miscellaneous					976,868	3.7
Group Total	9,455,800	14.2	8,114,529	0.2	8,098,702	31.4
<b>Metal</b>						
Optical goods, novelties, etc.					2,211,465	8.5
Industrial alloys, etc.					1,699,399	6.6
Dental alloys, etc.					501,802	1.9
Miscellaneous					5,950	0.2
Group Total	4,667,650	5.3	4,419,586	0	4,418,616	17.2
Grand Total	37,238,683	30.7	25,826,554	0.2	25,787,759	100.0

The next cycle is the one created by small neighborhood sweeps plants that are probably missed in any census return. The tonnages are presumably too small to cause serious errors.

Thirdly, there is the normal one of sending mill scrap to a retreatment plant. This is the cycle which is given in detail in the Bureau of Mines tabulations and which has been allowed for by Handy & Harman. The percentages in some industries are very high but of little significance, inasmuch as the turnover is rapid and the losses very small. The Bureau places this figure at about 31 per cent of the gross intake and Handy & Harman a little higher.

Then we come to the consumer scrap cycle. For instance a movie studio will recover most of the silver used in its photographic work. Finally we have the longest cycle, that of the hoarder who only enters the scrap market when he prefers cash to his holdings. To a minor

extent he balances himself out in that when he is prosperous he buys luxuries beyond his needs.

While mill is a very heavy item, amounting to return to the smelter of about a third of the gross purchases, consumer scrap is surprisingly

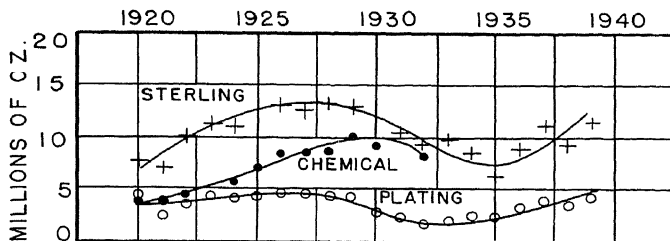


FIGURE 4. Net silver consumption in the United States and Canada (Handy and Harman).

small with the very serious exception of the photographic industry. The amount of used sterlingware reaching scrap treatment plants averages only about 500,000 ounces a year, or less than 5 per cent of the new sterling sold. There is virtually no recovery from used plated ware. In the chemical industry there is no significant recovery except in photography where, at a guess, there may be a film and hypo return of 50 per cent. In jewelry, alloys and miscellaneous there is some recovery of unknown amount.

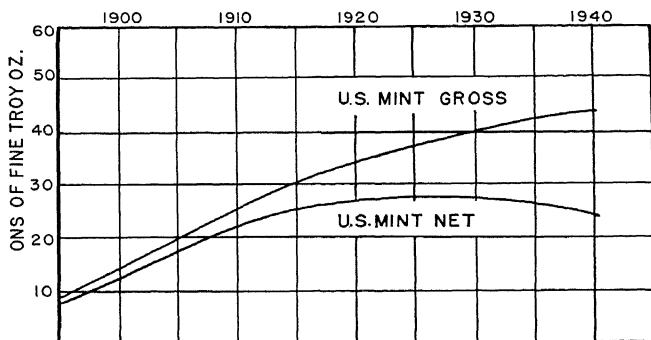


FIGURE 5. Annual industrial consumption of silver in the United States.

In Figure 5 the gross "trend" in Figure 1 is corrected for the scrap indicated in Figure 2. It will be noted that the resultant curve suggests an actual falling off in net consumption lately. In recent years the Handy & Harman net averages some 6,000,000 ounces higher than the



Mint net which is a measure of consumer's scrap plus the operations of the long-time hoarder.

It is always a temptation to torture statistics in an attempt to make them talk, but about all we can conclude is that the United States has an apparent consumption of about 25,000,000 to 30,000,000 fine Troy ounces a year, of which probably 70 per cent disappears from the scene, although considerably more must be accumulating in theoretically recoverable hoards.

# Chapter 20

## Summary and Conclusions

BY LAWRENCE ADDICKS

The foregoing chapters record an attempt to lay a broad foundation of information upon which others may build in developing silver as an industrial metal. The presentation has both the merits and the defects of multiple authorship; no attempt has been made to achieve unity of style. The subject matter ranges from the recital of well-known applications of silver to pure speculation. From the whole, certain more or less obvious conclusions may be drawn.

(1) Statistically silver is in bad health. Production is increasing due to causes originating largely in the economics of a group of other metals and not therefore self-corrective. The traditional function of silver as treasure is fast dwindling and increased industrial use is seemingly the only remedy in sight.

(2) Major increases in the amount of silver now used industrially will be needed to take up the surplus which in the last few years would have sent the price tumbling had it not been for the very large temporary purchases by the United States Treasury.

(3) Within limits, the price of silver is not the key to industrial consumption. Without doubt a market collapse due to forcing by-product production beyond consumptive demand would stimulate industrial use, but probably most of the new field could have been occupied at the former price, given sufficient public interest. From the producers' point of view—fundamental to this book—technical and commercial research and not price-cutting should be the solution.

(4) The effect of lower prices on the expansion of sterlingware and the decorative field generally would be quite inadequate. Doubling such consumption would add but some 15,000,000 ounces a year whereas perhaps 100,000,000 ounces is required to create a sound situation.

(5) The technical field may be subdivided into four groups: (a) metallurgical, (b) chemical, (c) electrical, and (d) biological.

(a) **Metallurgical.** The greatest hopes for large new consumption lie in this division. The properties of pure silver are such that probably only the psychological barrier created by its inclusion in the precious metal "ounce" class has impeded major expansion long ago. The container field, both metallic and non-metallic, is enormous, and all sorts of chemical ware, from ceramic and glass to rubber and ferro-alloy, have come into use in recent years while silver has been neglected. That is

why so much space has been devoted to the production of pure silver coatings and the corrosion resistance attainable by their use. This is easily the most promising field for immediate development.

Perhaps the ideal solution to the whole problem would be the discovery that a small addition of silver to some largely used metal or alloy would markedly improve its qualities. The chapter on alloys gives evidence that this search was carried out with zeal but without making any real killing. However, work being done outside of the group, such as the effects of additions of silver to stainless steel recently announced, may prove to have large tonnage possibilities. Also, a number of silver-poor alloys have been found to have salable properties and these in the aggregate will account for a considerable tonnage possibility. It seems probable that silver bearings have a bright future and other applications of the silver-rich alloys will contribute their bit.

**(b) Chemical.** There is a negative value to silver's chemical aloofness and this has been dealt with in the chapter on corrosion. This extends beyond mere serviceability into the preservation of fragrance and flavor. Some suggestive data on silver as a catalyst has been presented, and the biological applications have a chemical angle. Photography is the outstanding chemical use, but it has arrived at adult stature and much of its importance is cancelled by ultimate scrap recovery. Considered strictly as reagents, no useful field for silver compounds has been unearthed.

**(c) Electrical.** The field of silver-bearing contacts is rapidly growing. Major researches are under way in various laboratories dealing with the difficult physico-chemical problems connected with tarnish, wear, metal transfer and sticking. When it is realized that even telephone contacts, though requiring but a few grains of silver to a unit, number in the billions in the system taken as a whole, a general adoption of silver can be seen able to account for many millions of ounces. The experiments in the collection of current through silver-bearing brushes are of practical importance; a real invasion of the generator brush field is quite possible. Altogether the use of silver for contacts may be said to be really just getting started.

**(d) Biological.** This is very inviting territory but the consumption possibilities are quite unknown. If the acknowledged antiseptic properties of silver can be adequately directed, a wide field is open in both medicine and agriculture as well as in manufacturing operations where biological control is essential. A vast amount of work needs to be done and it is yet too early to make an intelligent appraisal.

Taking these groups jointly, it seems safe to say that the tonnage possibilities to solve the silver problem exist; that the industrial demand will steadily grow, regardless of the momentary price of the metal; and that this growth will be along the newer lines discussed rather than in the old established uses. An addition of 100,000,000 ounces a year to the present 50,000,000 ounces annual world consumption is a large order.

While intensive pressure along all the indicated lines of attack will be necessary to achieve it, there is no evidence justifying an attitude of defeatism. Perhaps the most dangerous pitfall lies in the development of consumers' scrap recovery; but that will take time and, in America at least, it is more natural to throw string into the wastebasket than to save it for next time.

This book is a record of an impure research undertaken to contribute to the resolution of a crisis. The measure of its success will lie not in what may or may not have been accomplished, but in the degree of interest aroused in those who have problems to solve where silver might be used. It probably contains much wishful thinking—but what worthwhile task has ever been accomplished without it?



## Appendix I. Bibliography

This bibliography, prepared at the National Bureau of Standards, is the result of a coöperative exchange of information between the silver research groups at the Bureau of Standards and the California Institute of Technology. The independent searches at the two institutions have been consolidated and arranged in sections which follow the previous chapter headings. Entries are listed in chronological order.

### National Bureau of Standards

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# Appendix I. Bibliography

## SECTION A. PHYSICAL AND CHEMICAL PROPERTIES OF SILVER

### CHAPTER 2

#### I. PHYSICAL PROPERTIES

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#### (5) Atomic and Ionic Radii

(included in 4 above)

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(See Appendix I, Section J)

### c. Catalytic

(See Appendix I, Section I)

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## SECTION B. ALLOYS

### CHAPTERS 3 AND 4

#### 1. ALUMINUM-SILVER

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## SECTION D.

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## 2. BRAZING ALLOYS, SOLDER

### CHAPTER 7

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### CHAPTER 8

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## SECTION G. CHEMICAL AND VAPORIZED COATINGS

### CHAPTER 11

#### 1. Chemical Reduction Methods

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## SECTION II. ELECTRICAL APPLICATIONS

## CHAPTERS 12 AND 13

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## SECTION I. CATALYTIC APPLICATIONS

## CHAPTER 14

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## SECTION J. CORROSION RESISTANCE OF SILVER

### CHAPTER 15

#### J. 1. Chemical Plant Applications and Corrosion Data (Exclusive of Tarnish)

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## SECTION K. BACTERICIDAL, FUNGICIDAL, AND RELATED PROPERTIES OF SILVER

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## SECTION L. PHOTOGRAPHIC APPLICATIONS AND RECOVERY OF SILVER

## CHAPTER 18

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- A. Fodor. The solutions of silver micelles by hydrogen peroxide. The absorptive binding or stoichiometric compounds of sols and precipitates of silver. *Kolloid Z.*, **39**, 173-178 (1926).
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- V. Moravek. Preparation of colloidal silver by reduction with chloroform. *Chem. Listy*, **19**, 195-203 (1925).
- C. A. Taylor. Silver Azide, an initiator of detonation. *Army Ordnance*, **5**, 824 (1925).
- R. Wyckoff. Crystal structure of silver phosphate and silver arsenate ( $\text{Ag}_3\text{XO}_4$ ). *Amer. J. Sci.*, **10**, 107-108 (1925).
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- G. Jones. Expansion-negative coefficient. *J.A.C.S.*, **81**, 191 (1909); *Sci. Abs.*, **12**, 224 (1909).
- G. F. Rodwell. On effect of heat on some chlorobrom iodides of silver. *Proc. Roy. Soc.*, **25**, 292 (1876); *Phil. Trans. Roy. Soc. London*, **173** (Pt. 3), 1125 (1882).

## Appendix II

### Patents Relating to Industrial Uses of Silver

The United States patents listed in this appendix have been assembled by the silver research group at the National Bureau of Standards. The foreign patents have been taken principally from lists furnished coöperatively by the rare metals research group at the California Institute of Technology.

## Appendix II

### Patents Relating to Industrial Uses of Silver

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# Appendix II. Patents

## SECTION I. SERIAL LIST OF U. S. PATENTS

Patent No.	Date	Patentee	Invention
25,206	8/23/1859	Martin; Improvement in Alloys	
81,576	9/1/1868	H. Ashcroft; Improved Non-corrosive Valve Seat	
104,879	6/28/1870	A. Plumb; Improved Composition: Amalgam for Filling Teeth	
139,078	10/25/1872	A. Lange; Improvement in the Manufacture of Springs for Watches and Other Time-pieces of Aluminum Compounds	
191,146	5/4/1876	W. Hubbell; Improvement in Metal Alloys for Commercial Coin	
196,262	10/16/1877	A. Stetefeldt; Improvement in Processes of Reducing Silver Ores	
209,263	2/7/1878	W. Hubbell; Improvement in Alloy for Coin	
211,630	1/28/1879	W. Hubbell; Improvement in Alloy for Coin	
219,265	9/2/1879	W. Hubbell; Improvement in Alloy Metals for Metric Silver Coin and Silverware	
295,456	3/18/1884	E. T. Starr; Secondary Battery and Method of Constructing Electrodes Therefor	
338,317	3/23/1886	O. M. Thowless; Alloy	
373,221	11/15/1887	C. C. Carroll; Alloy	
384,731	6/19/1888	C. W. Ward; Alloy	
385,955	7/10/1888	D. O'Hara, D. W. Eldredge, and J. Logan; Alloy	
429,157	6/3/1890	S. Singley; Anti-friction Alloy	
475,382	5/24/1892	C. C. Carroll; Composition of Matter and Method of Producing	
480,445	8/9/1892	C. F. Whitney; Aluminum Alloy	
489,790	1/10/1893	C. F. Carpenter; Non-magnetic Watch-balance	
526,147	9/18/1894	T. A. Edison; Art of Plating One Material with Another	
581,775	5/4/1897	C. Schwabe; Process of Depositing Metals on Silver Coatings	
712,027	10/28/1902	W. H. Walker; Alloy of Silver	
799,218	9/12/05	C. F. Blackledge; Process of Depositing Metal on Non-metallic Bodies	
808,453	12/26/05	A. E. Hobson; Silver Alloy	
906,229	12/8/08	C. H. von Hoessle; Process of Mirroring Glass or Like Surfaces	
929,582	7/27/09	E. Garretson; Electric-current Rectifier	
937,284	10/19/09	E. B. Craft and J. W. Harris; Alloy	
1,022,600	4/9/12	A. J. Rossi; Alloys of the Precious Metals and Method of Increasing Hardness	
1,023,332	4/16/12	A. J. Rossi; Alloys of the Precious Metals and Method of Increasing Hardness	
1,024,476	4/23/12	A. J. Rossi; Article Composed Essentially of Titanium and Silver and Method of Producing	
1,025,426	5/7/12	A. J. Rossi; Article Composed Essentially of Titanium and Silver and Method of Producing	
1,037,469	9/3/12	H. E. Goldberg; Process of Metallizing Electrotpe-molds	
1,076,137	10/21/13	W. A. McAdams; Aluminum Alloy and Method of Producing	
1,092,500	4/7/14	W. A. McAdams; Aluminum Alloy	
1,099,561	6/9/14	W. A. McAdams; Aluminum Alloy	
1,075,642	10/14/13	E. D. Gleason; Sterling Silver	
1,101,534	6/30/14	R. R. Graf; Alloy	
1,103,482	7/14/14	C. Canzler and R. Samersreuther; Alloy for Welding Copper and Nickel	
1,104,369	7/21/14	W. A. McAdams; Aluminum Alloy	
1,121,268	12/15/14	W. A. McAdams; Aluminum Alloy	
1,133,019	3/23/15	E. D. Gleason; Process of Making Alloys	
1,146,185	7/13/15	W. A. McAdams; Aluminum Alloy	
1,149,850	8/10/15	O. I. Metzger; Composition of Matter to be Used for Jewelry, Pins, Metal-lie Springs, and Other Metallic Articles	
1,164,907	12/21/15	T. J. Davis; Dental Amalgam	
1,166,129	12/28/15	P. R. Heyl; Terminal for Contact or Spark Devices.	
1,169,658	1/25/16	L. Lorentowicz; Method for Repairing Scored Cylinders	
1,181,742	5/2/16	W. D. Coolidge; Electrical Contact	
1,191,572	7/18/16	C. T. Davis; Surgical Package and Method for Indicating Sterilization Thereof	
1,191,890	7/18/16	E. D. Gleason; Sterling Silver.	
1,208,507	12/12/16	A. Dalby; Preparation for Silvering or Gilding Metal Articles	
1,215,138	2/6/17	T. S. Fuller; Brazing Material	
1,219,466	3/13/17	H. C. Kirk, Jr., and G. H. Dumlér; Method of Manufacturing Metal Articles by Deposit	
1,222,158	4/10/17	C. A. Stewart; Aluminum-soldering compound	
1,223,322	4/17/17	C. L. Gebauer; Process of Producing Metal Bodies	
1,229,037	6/5/17	H. S. Cooper; Metal Alloy	
1,239,195	9/4/17	L. Lorentowicz; Composition for Repairing Scored Cylinders	
1,247,977	11/27/17	W. A. McAdams; Aluminum Alloy	
1,248,621	12/4/17	H. S. Cooper; Metal Alloy	

Patent No.	Date	Patentee	Invention
1,263,656	4/23/18	F. A. Fahrenwald;	Process of Coating or Joining Articles of Tungsten or Molybdenum
1,283,284	10/29/18	W. E. Mowrey;	Precious-metal Alloy
1,296,938	3/11/19	F. A. Fahrenwald;	Composition of Matter for Platinum Substitute
1,301,633	4/22/19	A. H. Alexandre;	Process of Soldering Aluminum
1,321,170	11/11/19	J. A. Weiger;	Metal Alloy
1,339,009	5/4/20	G. L. van Allen;	Alloy
1,346,192	7/13/20	C. L. Gebauer;	Composition of Matter
1,357,000	10/26/20	C. S. Piggot;	Catalytic Acceleration of Oxidation Process
1,357,272	11/2/20	F. E. Carter;	Alloy
1,358,908	11/16/20	J. A. Williams;	Alloy for Electrical Contact-points
1,362,455	12/14/20	L. T. and F. Wallen;	Point for Electrical Contacts of Ignition Apparatus
1,375,552	4/19/21	W. Bocchetti;	Silver-solder
1,383,059	6/28/21	G. C. Bailey and A. E. Craver;	Process of Producing Formaldehyde
1,385,995	8/30/21	F. A. Fahrenwald;	Process of Synthesizing Ammonia in the Presence of a Catalytic Alloy
1,396,495	11/8/21	A. J. Baezwin;	Composition
1,415,925	5/16/22	P. de Clamecy;	Composition of Matter for and Method of Soldering and Welding Aluminum
1,416,929	5/23/22	W. E. Bailey;	Art of Electrolysis
1,425,935	8/15/22	N. B. Aukerman;	Process of and Means for Recovering Silver from Photographic and Other Baths
1,431,131	10/3/22	C. E. Hansen;	Composition White Metal
1,436,844	11/28/22	F. L. White;	Alloy for Electrical Contacts and Method for Making
1,443,475	3/13/23	L. Weisberg;	Recovering of Silver Used in Photographic Work
1,455,531	5/15/23	A. S. Hyman;	Alloy
1,466,061	8/28/23	O. Rebello;	Homogeneous Aluminum Solder
1,473,331	11/6/23	H. Bechhold;	Filter
1,483,327	2/12/24	W. C. Belus;	Alloy Flux for Soldering Aluminum and Process for Forming
1,501,049	7/15/24	A. Harper;	Process for Plating Stainless Steel and Articles Produced Thereby
1,515,658	11/18/24	T. C. Cole;	Process for Coating Aluminum
1,523,015	1/13/25	E. J. Guay;	Metal Mirror
1,527,942	2/24/25	L. Weisberg;	Recovery of Silver from Solutions Used in Photographic Work and Regeneration of Such Solutions for Further Use
1,533,246	5/19/25	E. F. Kingsbury;	Metallic Composition
1,533,944	5/26/25	T. B. and T. H. Lashar;	Silver Reinforced Silver-plated Flatware for Table Use
1,539,810	5/26/25	R. T. Gillette;	Welding Electrode
1,545,941	7/14/25	E. A. Coady;	Art of Electroplating
1,545,942	7/14/25	F. Conlin;	Electroplating
1,548,432	8/4/25	C. Belous;	Method of Electroplating Musical Instruments
1,551,618	9/1/25	A. Pacz;	Coated Aluminum Articles and Process and Means for Producing
1,552,184	9/1/25	H. Adams;	Metal Composition and Method of Manufacture
1,557,234	10/13/25	H. Bechhold;	Filter
1,557,235	10/13/25	H. Bechhold;	Filter
1,557,431	10/13/25	V. D. Davignon;	Gold Alloy and Method of Making
1,560,659	11/10/25	E. M. Burket;	Cleansing and Polishing Compound
1,561,247	11/10/25	E. F. Kingsbury;	Metallic Composition
1,561,650	11/17/25	T. H. Lashar;	Antitarnish Composition
1,563,079	11/24/25	C. A. Fontane;	Alloy
1,564,786	12/8/25	C. M. Hemen;	Composition for Cleaning and Polishing Silver
1,565,115	12/8/25	J. B. Speed and A. H. Falk;	Solder
1,574,544	2/23/26	B. Bart;	Method of Depositing Silver
1,574,714	2/23/26	C. C. Vogt;	Dental Alloy and Process of Making
1,579,431	4/6/26	V. E. Hybinette;	Light Aluminum Alloy and Method of Producing
1,579,819	4/6/26	C. G. King;	Seamless Plated Wire
1,580,443	4/13/26	T. P. Shields;	Gold Alloy
1,580,444	4/13/26	T. P. Shields;	Metallic Alloy
1,583,268	5/4/26	B. Bart;	Method of Forming Reflecting Surfaces
1,590,091	6/22/26	F. Heusler;	Silver Alloy
1,593,998	7/27/26	B. Bart;	Method of Depositing Silver
1,605,432	11/2/26	H. M. Fredriksen;	Alloy and Process of Forming
1,612,732	12/23/26	C. C. Vogt and J. W. Harsch;	Dental Alloy and Process of Making
1,614,752	1/13/27	W. L. Mitchell;	Silver Alloy and Method of Making
1,626,033	4/26/27	W. S. Ireland;	Alloy
1,626,925	5/3/27	V. Fener;	Alloy
1,628,610	5/10/27	F. E. Osborne;	Paper for Preventing Tarnishing of Polished Metals
1,628,673	5/17/27	R. H. Leach;	Silver Alloy
1,641,745	9/6/27	P. C. Dimberg;	Method of Uniting Blades
1,642,039	9/13/27	A. Schreier;	Process and Material for Sterilization of Liquids
1,643,304	9/27/27	M. G. Korsunsky;	Silver-Silicon Alloy and Process of Making
1,646,842	10/25/27	C. A. Whiting;	Method of Making Intermeshing Links
1,648,504	11/8/27	L. Offenbacher;	Apparatus for Producing a Silver Coating on Glass
1,651,662	12/6/27	C. W. Balke;	Tungsten Welding
1,658,713	2/7/28	T. S. Fuller;	Electrical Contact
1,685,204	9/25/28	A. Schreier;	Liquid-treating Material and Method of Making Same
1,687,056	10/9/28	R. Carl;	Process of Electrolytically Separating the Alloys of Silver with Other Precious or Base Metals
1,691,207	11/13/28	A. Pacz;	Process of Refining Metals and Alloys
1,691,324	11/13/28	V. K. Zworykin;	Television System

Patent No.	Date	Patentee	Invention
1,699,761	1/22/29	J. Silberstein; Solder	
1,712,244	5/7/29	E. G. Bok and E. Thoma; Process of Finishing Metal Articles and the Product Thereof	
1,717,250	6/11/29	J. J. Phelan; Brazing Flux	
1,719,365	7/2/29	D. Gray, R. O. Bailey, and W. S. Murray; Tarnish-resisting Silver and Silver Plate and Processes for Producing	
1,720,215	7/9/29	D. Gray, R. O. Bailey, and W. S. Murray; Method of Producing Tarnish-resisting Silver and Silver Plate	
1,720,216	7/9/29	D. Gray, R. O. Bailey, and W. S. Murray; Tarnish-resisting Silver Plate and Process for Producing	
1,720,894	7/16/29	D. Gray, R. O. Bailey, and W. S. Murray; Tarnish-resisting Silver Alloy, Etc., and Process for Producing	
1,724,204	8/13/29	B. F. Kelly; Process of Silvering and Beveling Small Mirrors	
1,731,210	10/8/29	V. D. Davignon; Gold Alloy	
1,731,211	10/8/29	V. D. Davignon; Gold Alloy	
1,731,212	10/8/29	V. D. Davignon; Gold Alloy	
1,731,213	10/8/29	V. D. Davignon; Gold Alloy	
1,732,727	10/22/29	A. J. Line; Aluminum Solder	
1,732,839	10/22/29	H. M. Fredrikson; Metal Alloy for Use in Manufacturing Electrical Contacts	
1,740,291	12/17/29	C. G. Fink and R. E. Lowe; Electrodes and Process for Making	
1,754,408	4/15/30	E. W. Stevens; Process and Apparatus for Separating Metallic Values	
1,757,507	5/6/30	M. E. Barker; Alloy	
1,757,508	5/6/30	M. E. Barker; Alloy	
1,758,293	5/13/30	W. S. Murray; Tarnish-resisting Silver and Silver Plate and Process for Producing	
1,758,651	5/13/30	J. R. Conover; Chemical Emulsion	
1,759,493	5/20/30	U. C. Tainton; Method of Electrolysis	
1,766,646	6/24/30	G. J. Jones; Method and Material for Preventing the Tarnishing of Silverware	
1,771,977	7/29/30	H. Blomberg; Wear-resisting Current-carrying Contact	
1,773,702	8/19/30	D. O. Bailey and W. S. Murray; Process for Producing Tarnish-resisting Silver and Silver Plate	
1,774,689	9/2/30	J. A. Williams; Material for Contact Points and the Like	
1,776,276	9/23/30	H. M. Williams; Electrical Apparatus	
1,779,809	10/28/30	D. Gray, R. O. Bailey, and W. S. Murray; Tarnish-resisting Silver and Silver Plate and Process for Producing	
1,782,092	11/18/30	D. Gray, R. O. Bailey, and W. S. Murray; Articles Having Tarnish-resisting Surface and Process of Making	
1,784,640	12/9/30	W. Noble; Poppet Valve	
1,789,854	1/20/31	L. E. Wemple and F. A. Warren; Zinc Alloy	
1,792,580	2/17/31	F. Feinreubel; Method for Producing Light Metal Pistons Running in Cylinders of Harder Material	
1,802,718	4/28/31	C. S. Jennings; Circuit-breaker Contact	
1,812,105	6/30/31	W. Matzka; Apparatus for the Sterilization of Liquids	
1,813,064	7/7/31	W. Matzka; Preserving Eggs	
1,816,476	7/28/31	C. G. Fink and W. G. King, Jr.; Manufacture of Double-walled Receptacles	
1,816,961	8/4/31	H. S. Cooper; Alloy and Method of Preparing	
1,822,682	9/8/31	J. A. Weiger; Valve Seat	
1,823,938	9/22/31	G. Henke; Process for the Production of Silver Plated Metal Articles Such as Table Requisites	
1,824,896	9/29/31	A. O. Jagger; Process of Producing Reduction Products of Carbon Monoxide	
1,829,668	10/27/31	W. Morrill; Aluminum Alloy	
1,829,963	11/3/31	R. H. Leach; Alloy	
1,833,723	11/24/31	W. E. Tunder; Alloy	
1,835,205	12/8/31	M. G. Corson; Alloy Composition	
1,835,965	12/8/31	J. J. Phelan; Brazing Flux	
1,838,130	12/29/31	S. Beckinsale; Magnetic Alloy	
1,838,633	12/29/31	A. Paez; Coloring Aluminum Alloys	
1,846,558	2/23/32	S. Jungmans; Process for Making Self Improving Aluminum Alloys	
1,846,733	2/23/32	G. Jones; Method of Cleaning Metals	
1,847,941	3/1/32	D. Gray, R. O. Bailey, and W. S. Murray; Metal Alloys and Process of Producing	
1,848,438	3/8/32	G. N. Sieger and J. A. Weiger; Alloy Material for Electrical Contacts	
1,850,594	3/22/32	W. Matzka; Process for Sterilization of Liquids	
1,850,997	3/29/32	P. Assmann; Production of Resistant Silver Surfaces	
1,851,219	3/29/32	U. C. Tainton; Method of Electrodeposition of Zinc	
1,857,507	5/10/32	K. G. D. Hickman and W. J. Winters; Process for the Separation of Silver by Electrolysis	
1,857,664	5/10/32	M. Schiffert; Treatment of Gold and Silver	
1,859,413	5/24/32	J. K. Smith; Alloy	
1,860,793	5/31/32	J. A. Weiger; Electrical Contacting Element	
1,863,612	6/21/32	Peter Assmann; Chemically Resistant Silver Alloy	
1,863,645	6/21/32	Peter Assmann; Chemically Resistant Silver Alloy	
1,866,699	7/12/32	F. Conlin; Brush for Electroplating and Electrocleaning and Anode for Use Thereof	
1,869,213	7/26/32	R. Teuts; Process of Separating Metals	
1,873,155	8/23/32	B. Scharnow; Ferromagnetic Materials	
1,875,911	9/6/32	W. Andrews; Welding of Copper	
1,882,114	10/11/32	G. H. Brady; Metal Alloy for Electric Contact Terminals	
1,883,420	10/18/32	H. C. Stephens; Method of Preserving Fruit Juices	
1,883,650	10/18/32	E. W. Eagle; Contact Material	
1,883,987	10/25/32	G. A. Krause; Sterilizing Container for Liquids	

Patent No.	Date	Patentee	Invention
1,885,232	11/1/32	W. H. Colbert; Mirror	
1,888,188	11/15/32	T. Tanabe; Stainless Silver Alloy	
1,891,495	12/20/32	W. H. Bassett, Jr., and R. H. Leach; Alloy	
1,892,051	12/27/32	D. Gray and B. K. Neher; Electroplated Chromium Article	
1,892,440	12/27/32	A. von Frankenberg; Centrifugal Casting Machine	
1,892,490	12/27/32	R. Heilmann; Dental Crown, Coated on the Front with Enamel, Made of Noble Metal or Noble Metal Material and Process for Its Production	
1,894,151	1/10/33	J. P. Bell; Sprue Wire	
1,894,669	1/17/33	F. Conlin; Method of Electroplating and Compositions for Use Therein	
1,894,670	1/17/33	F. Conlin; Method of Electrocleaning	
1,896,410	2/7/33	R. H. Leach; Tarnish Resistant Alloy	
1,898,618	2/21/33	F. Conlin; Process and Apparatus for Electroplating	
1,899,465	2/28/33	O. Kamps; Aluminum Alloy	
1,899,701	2/28/33	R. H. Leach; Alloy	
1,899,878	2/28/33	R. H. Leach; Alloy	
1,900,192	3/25/33	R. Oelberger; Alloy of Nickel, Silver, Tin, and Copper	
1,900,880	4/18/33	H. Gockel; Preparation of Metallic Coatings	
1,904,241	4/18/33	E. Kammerer; Compound Metal Stock	
1,905,467	4/25/33	K. C. D. Hickman; Method for Photographic Processing	
1,906,689	5/2/33	K. K. Ledig; Nib for Gold Pen-points	
1,908,222	5/9/33	F. Conlin; Brush for Electrolytic Use and Electrodes Therefor	
1,910,309	5/23/33	W. S. Smith, H. J. Garnett, and W. F. Randall; Magnetic Alloy	
1,913,423	6/13/33	E. M. Wise; Precious Metal Alloy	
1,917,378	7/11/33	L. Lenfant; Gold Alloy	
1,921,416	8/8/33	R. H. Leach; Alloy	
1,921,417	8/8/33	R. H. Leach; Alloy	
1,921,418	8/8/33	R. H. Leach; Alloy	
1,921,760	8/8/33	R. H. Leach; Alloy	
1,922,887	8/15/33	J. H. Müller; Silver Plating Compound and Method of Silver Plating	
1,924,097	8/29/33	J. Aderer; Alloy	
1,925,973	9/5/33	H. S. Cooper; Alloy and Article Composed of Same	
1,928,429	9/26/33	R. H. Leach; Alloy	
1,930,119	10/10/33	R. R. Bayes; Dental Alloy for Cast Dentures	
1,932,673	10/31/33	S. Ruben; Electrical Contact Element	
1,934,780	11/14/33	W. S. Murray and D. Gray; Intimate Mixture or Alloy	
1,935,520	11/14/33	W. Peacock, Jr.; Silver-copper Alloy Mirror and Method of Producing Silver-copper Alloy Film	
1,935,897	11/21/33	E. M. Wise; Precious Metal Alloy	
1,936,833	11/21/33	F. Maulen; Pin for Artificial Teeth	
1,940,962	12/26/33	L. H. Matthias; Contact for Electrical Circuit Breaker Mechanisms	
1,941,039	12/26/33	A. Luschenowsky; Magnesium Alloy	
1,941,376	12/26/33	E. A. Winkler; Electrolytic Apparatus	
1,941,438	12/26/33	K. Kiefer; Process for Metallizing with Reflecting Surface Celluloid Sheets and Other Forms by Chemical Means	
1,942,686	1/9/34	G. F. Colbert and W. H. Colbert; Mirror and Process of Making	
1,945,267	1/30/34	F. P. Fieldler and A. O. Jager; Contact Sulphuric Acid Process	
1,946,231	2/6/34	L. Nowack; Process for the Manufacture of Alloys of Precious Metals which are Amenable to Heat Treatment	
1,947,180	2/13/34	B. Bart; Tarnish-resisting Silver	
1,947,938	2/20/34	E. Hey; Process of Making a New Composition of Matter and the Product Thereof	
1,949,781	3/6/34	A. D. Champlin; Tarnish-proof Cloth	
1,951,280	3/20/34	W. G. Hale and W. S. Hickman; Cyclic Oxidation of Alcohols to form Aliphatic Acids	
1,952,082	3/27/34	R. H. Leach; Alloy	
1,952,083	3/27/34	R. H. Leach; Alloy	
1,954,316	4/10/34	K. C. D. Hickman and W. J. Weyerts; Method for the Recovery of Silver from Used Photographic Fixing Solutions by Electrolysis	
1,954,951	4/17/34	R. C. Rutherford; Method and Apparatus for Refining Metals	
1,955,211	4/17/34	C. H. von Hoessle; Method of Producing Colloidal Solutions of Inorganic Substances in Polyalcohols, and Products Obtained Thereby	
1,959,531	5/22/34	K. C. D. Hickman and W. J. Weyerts; Apparatus for Electroplating Silver from Used Photographic Fixing Solutions	
1,962,859	6/12/34	C. Dietz and J. O. Whiteley; Compound Wire	
1,963,085	6/19/34	A. W. Gray; Commutated Alloy	
1,963,333	6/19/34	C. A. Morales; Carrier	
1,965,012	7/3/34	N. O. Taylor; Precious Metal Alloy Composition	
1,965,093	7/3/34	J. Aderer; Alloy	
1,968,552	7/31/34	H. A. Bond and L. B. Smith; Oxidation of Alcohols	
1,969,018	8/7/34	R. H. Leach; Alloy	
1,969,019	8/7/34	R. H. Leach; Alloy	
1,969,705	8/7/34	R. P. De Vries; Ferrous Alloy	
1,970,034	8/14/34	O. Feussner; Electrical Resistance Thermometer	
1,970,318	8/14/34	E. F. Kern; Silver Alloy	
1,970,319	8/14/34	E. F. Kern; Silver Alloy	
1,975,113	10/2/34	G. Masing and O. Dahl; Heat Treatment of Copper-Beryllium Alloys	
1,975,114	10/2/34	G. Masing and O. Dahl; Manufacture of Springs	
1,975,115	10/2/34	G. Masing and O. Dahl; Article Subject to Abrasion	
1,976,790	10/16/34	W. K. Lewis and P. K. Frilich; Process of Oxidizing Hydrocarbons	
1,977,625	10/23/34	A. H. Ernst; Process of Decorating Glass	
1,977,639	10/23/34	S. C. Langdon; Metal Protected Mirror	

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1,978,516	10/30/34	J. A. Weiger and J. S. Williams;	X-ray Target
1,982,774	12/4/34	F. Winkler, E. Hochheim, and F. Bergmann;	Mirror
1,982,812	12/4/34	C. V. Fredelt;	Contact Material
1,984,151	12/11/34	R. E. Paine;	Alloy
1,984,203	12/11/34	G. N. Sieger;	Hard Metallic Composition and Contacts Thereof
1,984,225	12/11/34	J. C. McFarland;	Age Hardening Silver of Sterling or Higher Standard
1,985,006	12/18/34	F. D. Wilson;	Phototube
1,986,209	1/1/35	F. J. Maas;	Copper Alloy for Bearings
1,986,210	1/1/35	F. J. Maas;	Copper Alloy for Conducting Electricity
1,986,224	1/1/35	V. H. Sanders;	Switch Contact
1,987,451	1/8/35	N. O. Taylor;	Precious Metal Alloy Composition
1,987,452	1/8/35	N. O. Taylor;	Precious Metal Alloy Composition
1,988,012	1/15/35	R. B. Mason;	Metal Deposits in Oxide Coatings
1,988,246	1/15/35	G. A. Krause;	Process for the Sterilization of Liquids
1,988,525	1/22/35	W. P. Tedham, A. Wood, and G. B. Baker;	Photoelectric Tube
1,989,764	2/5/35	M. Meltner;	Process and Composition for the Production of Reflecting Surfaces
1,990,985	4/9/35	W. Truette;	Process for Parting Residues, Sweepings, and the Like Containing Precious Metals
1,990,783	2/12/35	C. B. Gwyn, Jr.;	Electrical Make-and-break Contactor and Method of Mounting Pivots Thereof
1,993,490	3/5/35	F. Strasser;	Aluminum Solder
1,994,112	3/12/35	W. Sanzenbacher;	Alloy
1,994,633	3/19/35	S. S. Boyd;	Solution and Method for Removing Silver from the Back of Mirrors
1,995,225	3/19/35	E. Raub;	Method of Preventing Tarnishing of Metal Articles
1,997,165	4/9/35	R. H. Brown;	Duplex Metal Article
1,997,166	4/9/35	R. H. Brown;	Duplex Metal Article
1,997,479	4/9/35	V. E. Burg;	Photoconductive Device and Method of Making
1,998,334	4/16/35	E. Rupp;	Electric Radiation Indicator
1,998,878	4/23/35	T. E. Lefort;	Process for the Production of Ethylene Oxide
1,999,864	4/30/35	E. A. Capillon and F. E. Carter;	Alloy
1,999,866	4/30/35	E. A. Capillon and F. E. Carter;	Alloy
2,000,310	5/7/35	H. G. White and F. L. Porter;	Method of and Means for Mirror Making
2,000,692	5/7/35	P. C. Dimberg;	Method of Uniting Nickel Chrome Steel Turbine Blades
2,001,017	5/14/35	O. Feussner and A. Jedelet;	Metal Article
2,001,134	5/14/35	C. Hardy;	Metal Powder
2,001,639	5/14/35	H. Turner;	Silver Solder
2,003,333	6/4/35	K. H. Burnard and H. F. Kane;	Method and Material for Preventing the Tarnishing of Silverware
2,003,467	6/4/35	W. Randolph and J. T. Ford;	Spark Plug Electrode
2,005,645	6/18/35	H. A. Bond and L. B. Smith;	Process of Oxidizing Aliphatic Alcohols to Aldehydes
2,006,859	7/2/35	H. W. Gillett;	Bearing Structure
2,008,131	7/16/35	W. Dieck and S. Schiff;	Process for Manufacturing Bactericidal Products and Resulting Product
2,008,282	7/16/35	W. H. Keen;	Chromium Plated Article and Method of Making
2,010,337	8/6/35	A. J. van Peski;	Process for Stabilizing Acid Liquor
2,010,805	8/13/35	M. Ow-Eschingen;	Process for the Production of Metal Coatings on Celluloid Substitutes
2,011,613	8/20/35	R. H. Brown and L. A. Willey;	Magnesium Duplex Metal
2,014,083	9/10/35	J. Johnson;	Alloy
2,015,004	9/24/35	J. W. Woolcock;	Production of Ketones
2,015,325	9/24/35	P. L. Spencer;	Vacuum Tube
2,015,345	9/24/35	R. H. Leach;	Alloy
2,015,751	10/1/35	G. D. Graves;	Catalytic Process for Producing Alicyclic Ketones
2,016,718	10/8/35	A. Hollar;	Method for Treating Bronze Wastes for Recovering Copper, Tin, Lead, and Precious Metals Therefrom
2,017,029	10/8/35	H. W. Kelley;	Glue and Method of Making
2,017,367	10/15/35	K. Kurz;	Method of Producing and Embossing Foil by Providing a Support Adapted to be Embossed with a Mirror Coating
2,018,916	10/29/35	G. A. Krause;	Sterilizing Liquids
2,019,419	10/29/35	W. A. Lazier;	Hydrogenation of Pyridine Bodies
2,019,984	11/5/35	R. H. Leach;	Alloy
2,020,949	11/12/35	R. H. Leach;	Alloy
2,021,828	11/19/35	A. S. Berry;	Solder Extruding Machine
2,021,885	11/26/35	J. C. Bird;	Process for Obtaining Colloidal Dispersions of Metals in Oils and Products Thereof
2,023,422	12/10/35	M. C. Huggett;	Method of Making Thermal Insulation
2,023,512	12/10/35	R. H. Brown;	Duplex Metal Article
2,024,150	12/17/35	E. H. Davignon;	Plated Metal and the Manufacture Thereof
2,024,545	12/17/35	J. R. Stack;	Dental Alloy
2,025,528	12/24/35	E. P. Schreiber;	Coating with Chromium
2,025,750	12/31/35	S. Loos;	Process of Producing Composite Dental Plates
2,026,209	12/31/35	P. H. Braas;	Copper Alloy
2,027,377	1/14/36	W. J. Hale;	Method of Converting Aldehydes to Acids
2,028,072	1/14/36	G. A. Krause;	Process for Preserving Milk
2,028,853	1/28/36	J. von Boese and K. Richter;	Method of Forming Thin Metallic Films by Cathode Disintegration



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2,030,476	2/11/36	H. E. Smith; Method of Producing Mirrors	
2,031,113	2/18/36	R. H. Leach; Alloys	
2,032,912	3/3/36	M. G. Corson; Process of Surface Hardening of Metals by Cementation with Antimony	
2,032,926	3/3/36	J. B. Ford; Electrical Contact	
2,033,161	3/10/36	W. E. Vail; Acid Synthesis Process	
2,033,709	3/10/36	F. R. Hensel and E. I. Larsen; Copper Alloys	
2,033,783	3/10/36	J. A. Payette; Pen Point	
2,037,446	4/14/36	J. A. Weiger; Electrical Make-and-break Contact	
2,039,372	5/5/36	P. A. Wickmann; Insulator	
2,039,880	5/5/36	F. A. Bull; Amalgam Filling for Teeth	
2,040,093	5/12/36	C. J. Malm and C. H. Fordyce; Nonalkali Metal Salts of Dicarboxylic Acid Esters of Cellulose	
2,040,806	5/12/36	F. Feigl; Substances Containing Silver and Methods of Producing	
2,041,184	5/19/36	L. L. Isenhour; Method for the Production of Furoic Acid	
2,041,381	5/19/36	J. S. Streicher; Pen Point	
2,041,667	5/19/36	J. E. Thomas; Mirror	
2,042,155	5/26/36	R. H. Leach; Alloy	
2,042,220	5/26/37	H. P. A. Groll and H. W. de Jong; Catalytic Oxidation of Unsaturated Alcohols	
2,042,534	6/2/36	G. A. Krause; Device for Treating Liquids	
2,043,966	6/9/36	H. W. Whiston; Apparatus for Depositing Metal by Electrode Dispersion	
2,045,080	6/23/36	M. Hagedorn; Manufacture of Molded Articles	
2,045,138	6/23/36	F. R. Hensel; Alloys	
2,045,637	6/30/36	J. H. de Boer and M. C. Teves; Phototube	
2,046,056	6/30/36	E. W. Bremer; Electrical Current Conductor	
2,046,380	7/7/36	F. R. Hensel; Copper Base Alloys	
2,046,467	7/7/36	G. A. Krause; Sterilization of Liquids by Means of Oligodynamy	
2,046,702	7/7/36	H. Scott; Copper Alloy	
2,047,302	7/14/36	C. A. Narkis; Snap Plug	
2,047,369	7/14/36	W. Hickok; Photoelectric Device	
2,047,371	7/14/36	H. E. Ives; Photoelectric Tube	
2,048,647	7/21/36	O. Feussner and A. Jedele; Process of Producing Hard Alloys	
2,048,648	7/21/36	O. Feussner and A. Jedele; Alloy and Process for Making	
2,049,472	8/4/36	W. Rosett; Cuprous Oxide Photoelectric Cell	
2,049,500	8/4/36	F. R. Hensel; Alloy	
2,049,771	8/4/36	C. B. Gwyn, Jr.; Method of Making Silver Contacts	
2,050,040	8/4/36	R. L. Coleman and K. Smith, Jr.; Dental Alloy	
2,050,077	8/4/36	E. M. Wise; Palladium Dental Alloy	
2,050,738	8/11/36	O. Fuchs and W. Querfurth; Process for the Production of Higher Alcohols from a Mixture of Ethyl Alcohol and Methyl Alcohol	
2,051,697	8/19/36	W. C. Garfield and R. H. Hieronymus; Liquid Cleaner for Silverware	
2,052,142	8/25/36	E. F. Kern; Silver Alloys	
2,052,143	8/25/36	E. F. Kern; Silver Alloys	
2,053,662	9/8/36	C. Hardy; Method of Making Electrical Conductors	
2,055,740	9/29/36	R. T. D. Williams; Bearing Metal Alloy	
2,057,604	10/13/36	L. Zickrick; Electrical Switch Contact	
2,058,429	10/27/36	H. W. Edwards; Mirror	
2,058,857	10/27/36	K. L. Emmert; Silver Base Alloy	
2,059,497	11/3/36	F. Strasser; Aluminum Solder	
2,060,530	11/10/36	A. F. Reilly; Electroplating	
2,060,977	11/17/36	J. H. de Boer; Photoelectric Device	
2,061,323	11/17/36	G. H. Meinzer; Apparatus for Sterilizing Aqueous Liquids	
2,061,617	11/24/36	F. B. Downing; Sulphonic Acid Derivatives of Aromatic Hydrocarbons Useful as Wetters and Cleansing Agents	
2,061,620	11/24/36	F. B. Downing; Sulphonated Derivatives of Aliphatic Hydrocarbons Useful as Wetters and Cleansing Agents	
2,061,624	11/24/36	C. B. Gwyn, Jr.; Silver Alloy	
2,062,116	11/24/36	J. O. Betterton and Y. E. Lebedoff; Process for Desilverizing Alloy of Lead and Tin	
2,062,226	11/24/36	K. Kurz; Method of Producing Embossing Foils	
2,063,034	12/8/36	E. Freund; Method of Producing Metallic Coatings on a Cellulose Ester Base	
2,063,365	12/8/36	C. Conover; Process for Manufacturing Monocarboxylic Acids	
2,064,060	12/15/36	G. Frenkel; Mirror and Display Device	
2,066,271	12/29/36	C. M. Irwin; Filter Material and Method of Making	
2,066,710	1/5/37	A. A. M. Bado; Purification of Water and Other Liquids	
2,066,878	1/5/37	J. H. de Boer and M. C. Teves; Photoelectric Tube and Process of Making	
2,067,507	1/12/37	G. O. Smith; Process of Treating Lead and Lead Alloys	
2,067,907	1/19/37	H. W. Edwards; Mirror, Process of Making, and Composition of Reflecting Element Therefor	
2,068,557	1/19/37	M. Massey; Rectifier	
2,070,271	2/9/37	C. B. Gwyn, Jr.; Electrical Contact	
2,070,321	2/9/37	L. F. Slezak; Electrical Contact for Rectifiers	
2,073,371	3/9/37	F. R. Hensel; Electrode for Welding	
2,073,522	3/9/37	K. H. Kingdon and H. E. Thomson; Photoelectric Tube	
2,073,621	3/16/37	J. M. Blaney; Method of Removal of Excess Halides from Photographic Developing Baths	
2,073,664	3/16/37	L. Weisberg and W. F. Greenwald; Regeneration of Photographic Developer Solutions	
2,075,477	3/30/37	R. D. Smith; Glass Closure for Metal Containers and Method of Making	

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2,075,492	3/30/37	J. G. Zimmerman	Storage Battery Plate
2,077,378	4/20/37	E. Duren	Process of Metal Coating Glass
2,077,442	4/20/37	W. F. Tedham and J. D. McGee	Cathode Ray Tube
2,077,683	4/20/37	A. J. McMaster and C. E. Purson	Photoelectric Tube
2,077,684	4/20/37	A. J. McMaster	Photoelectric Tube
2,079,477	5/4/37	S. Asao and M. Nagashima	Photoelectric Tube
2,079,600	5/11/37	R. O. Grisdale	Method of Making Resistance Devices
2,079,784	5/11/37	R. C. Williams	Plating by Thermal Evaporation
2,080,811	5/18/37	K. L. Emmert	Electrical Contact
2,082,102	6/1/37	J. R. Fisher	Resistance Element
2,083,052	6/8/37	E. L. Chott	Dental Alloy and Method of Making
2,084,928	6/22/37	H. Turner	Silver Solder
2,086,324	7/6/37	P. Feremutsch	Sterilizing Liquids
2,087,716	7/20/37	C. Banseher	Method of Soldering Aluminum or Aluminum Alloys
2,091,259	8/31/37	J. R. Fisher	Resistance Unit
2,092,449	9/7/37	O. Fuchs	Manufacture of Condensation Products from Aliphatic Organic Compounds
2,094,482	9/28/37	W. J. Weder	Art of Uniting Metals
2,094,483	9/28/37	W. J. Weder	Art of Uniting Metals
2,094,784	10/5/37	E. W. Bremer	Resistance Welding Electrode
2,095,781	10/12/37	F. D. Wilson	Photosensitive Device
2,095,820	10/12/37	W. Lenz	Control Mechanism for Multiple Hydraulic Gears
2,095,890	10/12/37	A. R. Powell and E. R. Box	Pen Nib
2,096,011	10/19/37	E. W. Smith	Method and Apparatus for the Treatment of Liquids
2,096,014	10/19/37	J. Tausz	Alloy
2,096,924	10/26/37	P. Schwarzkopf	Composite Structural Product and Method of Making
2,098,300	11/9/37	D. T. May	Electric Welding
2,098,879	11/9/37	A. R. Powell	Alloy for Dental Plates
2,099,551	11/16/37	L. Zickrick	Electrical Switch Contacts
2,099,582	11/16/37	I. R. Valentine	Brazing Flux
2,100,314	11/30/37	O. E. Harder	Liner for Bearings
2,101,065	12/7/37	C. I. Hayes	Heat Treatment Furnace
2,101,118	12/7/37	H. L. Whitman	Aluminum Alloy
2,101,759	12/7/37	C. F. Smart	Bearing
2,102,448	12/14/37	H. L. Whitman	Process of Preparing Aluminum Alloys
2,102,700	12/21/37	G. R. Stilwell	Photoelectric Tube
2,102,908	12/21/37	E. R. Darby and P. J. Potter	Liner for Bearings
2,103,267	12/28/37	A. J. Mandell	Alloy for Vacuum Tube Elements
2,103,538	12/28/37	F. P. Kolb	Reflector
2,105,352	1/11/38	H. H. Harris	Metal Surface
2,105,440	1/11/38	B. C. Miller	Manufacture of Metal Coated Paper
2,105,835	1/18/38	G. A. Krause	Sterilizing Liquid
2,107,094	2/1/38	O. A. Townsend and A. P. Masters	Colored Photography
2,108,700	2/15/38	R. H. Adey	Apparatus for the Electrodeposition of Metals
2,109,151	2/22/38	G. A. Krause	Process for Artificially Aging Alcoholic Liquids and Perfumes
2,110,792	3/8/38	B. Egeberg and N. Promisel	Process for Electrodeposition of Silver and Products Obtained Therefrom
2,110,930	3/15/38	H. G. Dollin	Reuperation of Valuable Metals from Photographic Baths
2,113,517	4/5/38	A. R. Powell and E. C. Davies	Electrodeposition of Silver
2,113,977	4/12/38	A. M. Barnes	Manufacture of Mirrors
2,116,252	5/3/38	H. H. Schwarzkopf	Alloys for Electrical Contacts and Electrodes
2,116,351	5/10/38	J. C. Ryan	Bearing Alloy
2,117,657	5/17/38	W. C. Gangloff and R. E. Hieronymus	Silver Tarnish Inhibitor
2,119,304	5/31/38	E. D. Viers and B. C. Case	Electroplating
2,119,965	6/7/38	H. H. Schwarzkopf	Alloy
2,120,203	6/7/38	D. J. Hood and J. H. Winterburg	Reducing Solution for the Deposition of Metallic Films
2,121,875	6/28/38	W. Kruse and M. J. Fischer	Process for Sterilizing and Disinfecting
2,123,024	7/5/38	E. R. Piore	Electrode for Electric Discharge Devices
2,123,330	7/12/38	O. Feussner and A. Jedele	Palladium Alloy
2,123,449	7/12/38	H. L. Whitman	Alloy
2,124,331	7/19/38	M. Boekmühl, E. Dürzbach, and W. Persch	Stable Colloidal Dispersion of Metals
2,125,228	7/26/38	O. E. Harder	Brazing Alloy
2,125,333	8/2/38	R. M. Carter	Production of Olefine Oxides
2,126,010	8/9/38	J. L. Haughton and W. E. Prytherch	Magnesium Alloy
2,126,386	8/9/38	F. R. Hensel and E. I. Larsen	Copper-Silver-Beryllium-Manganese Alloy
2,126,633	8/9/38	F. R. Hensel and E. I. Larsen	Copper-Silver Alloys
2,126,635	8/9/38	E. Hopkins	Teleticket System
2,126,737	8/16/38	G. J. Comstock	Manufacture of Articles from Powdered Materials
2,127,676	8/23/38	C. H. Coleman	Process of Tempering Gold and Silver Alloys
2,128,582	8/30/38	B. C. Gardiner	Photoelectric Surface
2,128,932	9/6/38	L. H. Fitch, Jr., and F. E. Fay	Preparation of Resinous Reaction Products of Sulphur Dioxide and Olefines
2,129,700	9/13/38	M. W. MacAfee	Solvent for Use in Treatment of Ores
2,129,721	9/13/38	E. M. Wise	Palladium-Silver-Platinum Alloys
2,131,104	9/27/38	F. R. Hensel and E. I. Larsen	Copper-Silver-Beryllium-Manganese Alloy
2,131,994	10/4/38	F. R. Hensel	Refractory Metal Composition
2,132,116	10/4/38	H. R. Klepe	Alloy
2,134,306	10/25/38	A. W. Lewis	Lubrication

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2,134,366	10/25/38	C. Hardy;	Production of Metal Sheets
2,135,480	11/8/38	C. Birdseye;	Reflecting Glow Lamp
2,135,875	11/8/38	F. L. Jones and R. J. Kirchmaier;	Process of Making Metal Reflectors
2,136,024	11/8/38	H. Schneider;	Process and Apparatus for Producing Metallic Coatings on Various Articles
2,136,483	11/15/38	K. E. Barnard and A. F. McLean;	Method and Material for Preventing the Tarnishing of Silverware
2,136,496	11/15/38	N. M. Petersen;	Finning Compound
2,136,655	11/15/38	J. G. Rippet;	Brass Alloy
2,136,915	11/15/38	K. L. Emmert;	Silver Alloys
2,136,918	11/15/38	F. R. Hensel and E. I. Larsen;	Copper Alloys
2,136,919	11/15/38	F. R. Hensel and E. I. Larsen;	Copper Alloy of Improved Characteristics
2,137,617	11/22/38	R. H. Imes and H. F. Fruth;	Electrical Contact and Method of Making the Same
2,138,088	11/29/38	E. A. Capillon;	Solder Filled Wire
2,138,599	11/29/38	C. B. Gwyn, Jr.;	Contact Element
2,138,637	11/29/38	R. H. Leach;	Alloys
2,138,638	11/29/38	R. H. Leach;	Alloys
2,138,729	11/29/38	W. T. Butcher;	Process of Alloying Metals with Lead
2,140,531	12/20/38	R. B. Kennedy;	Aluminum Alloy Solders
2,141,113	12/20/38	C. Peterson;	Contact
2,141,114	12/20/38	C. Peterson;	Contact
2,141,156	12/20/38	A. W. Peterson;	Alloy
2,141,157	12/20/38	A. W. Peterson;	Alloy
2,141,201	12/27/38	Jeno Tausz;	Alloy
2,142,104	1/3/39	C. Birdseye;	Electric Lamp
2,143,217	1/10/39	W. Truthe;	Process for Reducing the Grain in Precious Metals and their Respective Alloys
2,143,723	1/10/39	C. H. Walker and C. Sykes;	Method and Apparatus for Applying Metal Coatings
2,143,914	1/17/39	F. R. Hensel and E. I. Larsen;	Copper-Silver-Beryllium-Nickel Alloy
2,143,915	1/17/39	G. Jobst;	Indirectly Heated Cathode
2,143,959	1/17/39	K. Schumpelt and E. O. Liebig;	Method of Forming Amalgam Films on Araldite Alloys
2,143,995	1/17/39	C. E. Nickerson;	Method of Producing a Colloid Relief on a Nickel Surface
2,144,044	1/17/39	C. Birdseye;	Reflecting Electric Lamp
2,144,279	1/17/39	H. L. Whitman;	Alloy
2,144,649	1/24/39	J. Eggert and G. Heymer;	Process of Printing Lenticular Film and Lenticular Film Thereof
2,144,673	1/24/39	C. Birdseye and P. Deren;	Incandescent Lamp and Its Manufacture
2,144,932	1/24/39	R. R. Porter;	Recovery of Silver from Argentio-Jarosite
2,145,248	1/31/39	T. B. Chace;	Method of Producing Steel Clad With a Copper Base Metal and the Product Thereof
2,145,651	1/31/39	C. J. Funk;	Composite Article and Method of Making
2,145,732	1/31/39	C. A. Nickle;	Mirror
2,146,025	2/7/39	F. M. Penning;	Coating by Cathode Disintegration
2,146,630	2/7/39	J. Johnson;	Alloys
2,146,722	2/14/39	E. R. Darby;	Spark Plug
2,147,672	2/21/39	R. Rodrian;	Smelting and Refining Process
2,148,040	2/21/39	P. Schwarzkopf;	Method of Manufacturing Composite Materials and Shaped Bodies Thereof
2,151,457	3/21/39	R. C. Williams;	Method of Coating Surfaces by Thermal Evaporation
2,151,567	3/21/39	H. J. Seeman;	Electrodes for Arc Discharge Valves
2,151,905	3/28/39	K. L. Emmert;	Electric Contact Combination
2,153,786	4/11/39	P. Alexander and A. de Dani;	Process and Apparatus for Thermal Deposition of Metals
2,153,928	4/11/39	J. D. Kendall;	Sensitized Photographic Emulsions
2,153,930	4/11/39	J. D. Kendall;	Sensitized Photographic Emulsion
2,154,052	4/11/39	E. G. Rolande;	Bear Dispensing Device
2,154,068	4/11/39	W. C. Ellis;	Electrical Contact
2,154,895	4/18/39	H. Fricke, K. Bitterfield, and J. Brunken;	Process of Hardening Protein Substances
2,155,475	4/25/39	W. Dieteler;	Sensitizing Silver Halide Emulsions
2,156,626	5/2/39	G. P. Ham;	Photographic Developing Medium Producing Fine Grain Results
2,156,914	5/2/39	A. L. Kaye, R. S. Williams, and J. Wulff;	Stainless Steel
2,157,121	5/9/39	E. R. Darby, L. A. Berera, and P. J. Potter;	Bearing Alloy
2,157,933	5/9/39	F. R. Hensel and K. L. Emmert;	Silver-Indium Contact
2,159,755	5/23/39	V. K. Zworykin and L. Meker;	Method and Apparatus for Detecting Heat
2,159,763	5/23/39	F. R. Hensel;	Metallic Composition
2,161,253	6/6/39	F. R. Hensel and K. L. Emmert;	Silver Contact
2,161,254	6/6/39	F. R. Hensel and K. L. Emmert;	Silver-Magnesium Contact
2,161,374	6/6/39	F. R. Hensel, K. L. Emmert, and J. W. Wiggs;	Silver Alloy
2,161,375	6/6/39	F. R. Hensel, K. L. Emmert, and J. W. Wiggs;	Silver Alloy
2,161,376	6/6/39	F. R. Hensel, K. L. Emmert, and J. W. Wiggs;	Silver Base Alloy
2,162,062	6/13/39	D. H. Corbin;	Manufacture of Spark Plugs
2,162,380	6/13/39	A. S. Doty and E. F. Swazy;	Metal Composition
2,162,627	6/13/39	A. R. MacGregor;	Alloy
2,162,909	6/20/39	E. L. Brinker and H. J. Gray;	Apparatus for Recovering Metals and Other Substances from Aqueous Liquids
2,163,224	6/20/39	P. P. Alexander;	Method of Production of Alloys

Patent No.	Date	Patentee	Invention
2,164,332	7/4/39	M. E. Macksound;	Apparatus for Applying Mirror Surfaces to the Interior of Lamp Bulbs
2,165,085	7/4/39	H. L. Whitman;	Alloy
2,165,338	7/11/39	L. G. S. Brooker and F. L. White;	Merocarboeyanine Dyes and Photographic Emulsions Containing the Same
2,165,481	7/11/39	F. R. Hensel and K. L. Emmert;	Electrical Make-and-break Contact
2,166,248	7/18/39	F. R. Hensel and K. L. Emmert;	Electrical Contacting Element
2,166,736	7/18/39	G. L. White and G. H. Keyes;	Photographic Emulsion
2,167,678	8/1/39	F. Purkardhofer and G. Battilana;	Solder
2,169,189	8/8/39	J. M. Kelly;	Copper Base Alloy
2,169,592	8/15/39	A. W. Peterson;	Alloy
2,170,451	8/22/39	H. H. Schwarzkopf;	Alloy
2,171,086	8/29/39	C. S. Gibson;	Preparation of Gold Films
2,171,697	9/5/39	F. R. Hensel and L. I. Larson;	Alloy
2,171,911	9/5/39	O. F. Bloch;	Antihalation Layer for Photographic Sensitive Materials
2,172,388	9/12/39	A. L. Kaye, R. S. Williams, and J. C. Wulff;	Stainless Steel
2,172,421	9/12/39	H. H. Uhlig;	Corrosion-resistant Ferrous Alloys
2,172,422	9/12/39	H. H. Uhlig;	Corrosion-resistant Ferrous Alloys
2,172,512	9/12/39	J. A. Kilgallon;	Precious Metal Alloy
2,175,899	10/10/39	J. M. Kelly;	Process for Making Metal Articles
2,177,257	10/24/39	L. Jakob and B. Wendt;	Colored Photographic Pictures
2,177,268	10/24/39	N. G. Schellenger;	Switch Terminal Construction
2,178,233	10/31/39	L. Klatzov;	Cathode Ray Tube
2,178,238	10/31/39	E. A. Massa and G. A. Morton;	Electric Discharge Device
2,178,508	10/31/39	L. Zickrick;	Electrical Switch Contact
2,178,573	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,578	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,579	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,580	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,581	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,582	11/7/39	J. A. Gann;	Magnesium Alloy
2,178,612	11/7/39	W. Schneider and M. Hagedorn;	Photographic Silver Halide Emulsion Layers
2,179,960	11/14/39	P. Schwarzkopf;	Agglutinated Material in Particular for Electrical Purposes and Shapes Thereof
2,183,202	12/12/39	P. Miscintelli;	Process for Obtaining Copper Linings
2,183,661	12/19/39	L. S. Trimble;	Process for Coloring Photographic Images
2,184,022	12/19/39	M. W. Seymour;	Color Photography
2,186,117	1/9/40	A. R. Lytle;	Filler Material for Welding
2,186,245	1/9/40	J. M. Kelly;	Electrical Contact Member
2,186,452	1/9/40	E. Freund and F. Deutsch;	Artificial Structure and Method of Preparing
2,187,377	1/16/40	F. R. Hensel;	Wear Resistant Electric Contact
2,187,378	1/16/40	F. R. Hensel;	Abrasion Resistant Electric Contact
2,187,379	1/16/40	F. R. Hensel and K. W. Emmert;	Alloy
2,188,681	1/30/40	J. R. Freeman, Jr., and A. W. Tracy;	Corrosion-resistant Copper-Zinc Alloy
2,189,571	2/8/40	C. S. Sivil and E. O. Liebig;	Alloys
2,189,755	2/15/40	F. R. Hensel;	Metal Composition
2,189,756	2/15/40	F. R. Hensel;	Molybdenum Composition
2,190,121	2/13/40	P. Miscintelli;	Process for Obtaining Copper Linings
2,190,477	2/13/40	F. R. Hensel;	Refractory Carbide Composition
2,190,528	2/13/40	D. K. Wright;	Electric Projection Device
2,194,056	3/19/40	J. Quaglia;	Recovery of Silver from Waste Hyposulphite Liquids.

## SECTION 2. ALLOYS

## (1) Aluminum-Silver

United States	
2,144,279	1,261,987
1,994,112	1,247,977
1,986,210	1,146,185
1,986,209	1,121,268
1,984,225	1,104,369
1,982,774	1,099,501
1,941,039	1,092,500
1,890,465	1,076,157
1,863,645	480,445
1,863,612	373,221
1,859,413	139,078
1,846,558	497,241
1,838,633	485,091
1,835,205	477,721
1,833,723	476,930
1,820,608	472,248
1,792,580	469,290
1,732,727	468,001
1,643,304	464,030
1,590,091	456,018
1,579,481	440,480
1,563,079	440,450
1,551,613	432,964
1,466,061	412,074
1,387,900	410,693

## (1) Continued

406,086	640,596
354,202	594,851
353,891	508,344
349,463	501,391
343,424	473,412
335,105	468,853
330,073	405,157
258,726	395,331
211,456	344,255
180,381	334,343
18,198	287,914
16,359	249,224
14,502	236,518
14,226	601,328
4,779	595,851
	542,238
819,263	541,105
797,714	514,126
795,722	512,986
789,617	496,348
780,773	496,348
772,586	496,348
739,035	456,343
700,091	399,020
695,858	392,811
689,206	271,848
663,173	230,095

## (1) Continued

204,543	Swiss	155,178
132,612		
	Italian	Swedish
328,640		68,921
298,571		Norwegian
	Japanese	52,193
		Canadian
102,000		321,779
91,228		Russian
36,520		25,595

## (2) Antimony-Silver

United States	
2,067,507	225,200
2,053,862	171,607
2,052,143	
2,052,142	695,658
2,032,912	613,511
1,984,225	548,932
1,970,319	497,932
1,970,318	496,348
1,643,304	
1,628,673	Swiss
	181,868
	British
467,676	
452,411	

## SECTION 2. ALLOYS (Continued)

## (3) Arsenic-Silver

German

496,349  
496,348

## (4) Barium-Silver

United States

1,925,978

British

496,033

## (5) Beryllium-Silver

United States

2,143,914  
2,136,919

British

1,859,413  
1,816,961456,018  
440,480440,450  
399,2612,094,784  
2,046,0562,031,113  
2,024,5452,020,949  
1,984,2251,963,085  
1,941,039

1,928,429

French

728,230

Canadian

345,629

Italian

342,591

Swiss

155,533

## (6) Bismuth-Silver

German

596,023  
575,926  
496,349

French

739,053  
699,068

## (7) Cadmium-Silver

United States

2,159,763  
2,141,2011,891,495  
1,645,3042,141,114  
2,141,1132,140,631  
2,138,0882,136,915  
2,136,6552,134,306  
2,125,2282,109,998  
2,101,7592,100,314  
2,099,5512,096,014  
2,080,8112,061,624  
2,059,4972,058,557  
2,055,7402,053,662  
2,052,1432,052,142  
2,049,5001,970,319  
1,970,3181,969,019  
1,969,0181,952,083  
1,952,0821,940,962  
1,921,7601,921,496  
1,921,4181,921,417  
1,899,8731,899,701  
1,896,410

1,896,410

British

831,256  
797,422  
792,568  
754,066  
747,789  
688,800  
667,121  
661,821  
659,668  
628,572  
46,598

German

575,926  
504,772  
496,348

Japanese

102,000  
99,246

Canadian

276,193

Austrian

141,479

## (8) Calcium-Silver

United States

1,970,318

British

464,030

## (9) Carbon-Silver

United States

1,984,203  
1,605,432

## (10) Cesium-Silver

United States

2,128,582  
2,123,024  
2,102,760  
2,077,643  
2,077,6332,077,442  
2,047,371  
2,045,637  
1,988,525  
1,985,006

## (11) Chromium-Silver

United States

2,049,500  
2,046,056  
2,045,138  
1,970,319  
1,970,3181,580,443  
1,574,714  
461,845  
626,084  
514,126  
474,387  
712,507

British

German

1,557,431  
1,466,061  
1,455,531  
1,375,552  
1,321,170  
1,215,138  
1,146,185626,084  
514,126  
474,387  
712,507

French

German

674,551  
626,996  
626,084  
625,251  
624,723  
622,580  
620,350  
596,023  
595,851  
584,172  
551,798  
541,105  
514,772  
499,677  
496,348  
474,887

British

Canadian

Austrian

Japanese

Italian

Indian

Russian

Norwegian

German

French

United States

1,963,085

761,496

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## (13) Continued

1,921,416  
1,917,378  
1,913,423  
1,899,873  
1,899,701  
1,892,490  
1,891,495  
1,883,650  
1,829,903  
1,789,854  
1,771,977  
1,757,507  
1,732,839  
1,731,213  
1,731,212  
1,731,211  
1,731,210  
1,612,782  
1,605,432  
1,580,444  
1,680,443  
1,574,714  
1,563,079  
1,557,431  
1,466,061  
1,455,531  
1,375,552  
1,321,170  
1,215,138  
1,146,185224,836  
221,770  
211,456  
209,975  
198,222  
171,607  
152,777

French

817,124  
810,388  
771,176  
761,496  
755,880  
746,755  
729,435  
722,280  
712,507  
709,850  
706,412  
700,091  
688,967  
632,368  
46,612  
46,598  
45,761

German

674,551  
626,996  
626,084  
625,251  
624,723  
622,580  
620,350  
596,023  
595,851  
584,172  
551,798  
541,105  
514,772  
499,677  
496,348  
474,887

British

Canadian

Austrian

Japanese

Italian

Indian

Russian

Norwegian

German

French

United States

1,963,085

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## (14) Gallium-Silver

United States

1,963,085

French

761,496

## (15) Germanium-Silver

United States

1,963,085

French

761,496

# APPENDIX II. PATENTS

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## SECTION 2. ALLOYS (Continued)

### (16) Gold-Silver

United States	209,975
2,141,157	157,884
2,141,156	152,277
2,127,676	
2,123,330	
2,050,077	811,305
2,050,040	805,717
2,048,648	771,176
2,048,647	765,243
2,042,155	755,880
2,025,759	746,755
2,001,017	741,215
1,987,452	729,435
1,987,451	722,280
1,970,084	712,507
1,965,093	48,121
1,965,012	
1,930,119	671,223
1,924,007	659,114
1,917,378	652,451
1,906,089	652,142
1,892,490	643,568
1,882,114	632,284
1,731,213	620,645
1,731,212	620,084
1,731,211	621,152
1,731,210	611,709
1,687,056	584,549
1,580,444	551,798
1,580,443	514,772
1,561,247	499,677
1,557,431	474,887
1,296,038	
1,248,621	154,703
	154,006
British	152,133
490,561	145,746
485,977	141,479
469,290	138,375
459,539	
456,018	23,266
455,985	22,764
444,754	
405,862	259,847
379,485	
372,236	109,226
280,073	
257,891	91,104
224,836	
	22,995

### (17) Indium-Silver

United States	French	761,496
1,987,452		
1,987,451	German	60,255
1,965,012		
1,963,085	Canadian	
1,934,730		338,197
1,847,941		

### (19) Iron-Silver

United States	440,480
2,172,422	440,450
2,172,421	431,511
2,172,388	430,989
2,156,914	425,455
2,144,279	355,456
2,123,330	324,009
2,070,271	224,836
2,048,647	186,381
1,989,705	
1,941,039	830,183
1,838,130	824,861
1,757,508	810,388
British	
496,774	787,234
451,101	778,185
450,619	728,230
450,431	
	658,887

### (19) Continued

613,511	Italian
584,549	
512,126	

### (21) Lead-Silver

United States	476,223
2,138,729	474,410
2,102,948	473,652
2,099,551	467,676
2,067,507	466,964
2,062,116	466,946
2,057,604	461,845
1,984,225	437,713
1,851,219	433,653
1,759,493	271,298
1,740,291	171,607
1,699,761	
1,358,908	French
1,296,938	831,256
1,222,158	746,755
	43,121
British	
509,949	German
505,949	649,958

### (22) Lithium-Silver

United States	
1,970,319	
1,970,318	

### (23) Magnesium-Silver

United States	British
2,178,582	497,241
2,178,581	477,721
2,178,580	464,030
2,178,579	458,324
2,178,578	456,018
2,178,573	412,074
2,126,386	
2,126,010	French
2,011,613	810,610
1,994,112	780,773
1,984,225	728,230
1,984,151	
1,941,039	German
1,784,840	548,238
1,731,213	541,105
1,731,212	496,348
1,731,211	
1,731,210	Australian
	20,172

### (24) Manganese-Silver

United States	414,213
2,144,279	406,086
2,141,114	290,565
2,141,113	211,456
2,131,104	
2,084,928	French
2,052,143	754,055
2,052,142	700,091
2,032,912	683,173
1,970,319	640,596
1,970,318	43,934
1,941,039	
1,863,645	German
1,850,997	659,658
1,590,091	628,572
1,574,714	613,511
	596,023
	548,238
	512,986
	496,348
British	
470,323	
457,785	Austrian
457,783	138,375
431,584	Hungarian
	109,226

### (25) Mercury-Silver

United States	British
2,094,483	492,088
2,094,482	476,375
2,083,052	German
2,039,880	626,645
2,024,545	Canadian
1,720,216	
1,720,215	Japanese
	353,526
	93,608
	41,481

### (26) Molybdenum-Silver

United States	French
2,057,604	792,568
1,986,210	
1,982,312	German
1,574,714	649,958
	643,567
	596,023
	474,887
British	
456,018	
437,713	
416,684	

### (27) Nickel-Silver

United States	258,108
2,159,763	234,836
2,144,279	198,222
2,136,915	186,381
2,080,811	
2,070,271	French
2,052,143	830,129
2,052,142	777,839
2,048,648	740,755
2,048,647	668,800
2,037,446	632,386
1,999,866	43,121
1,999,864	German
1,970,319	652,451
1,970,318	626,084
1,969,019	596,023
1,969,018	514,126
1,936,333	474,887
1,925,978	Canadian
1,896,410	315,801
1,883,650	276,493
1,757,508	259,845
1,757,507	
1,561,247	Japanese
1,455,531	
	110,779
	36,520
	497,241
	451,101
	440,450
	434,192
	399,281
	361,041
	359,014
	343,309
	259,108
	British
	Russian
	29,594
	Italian
	319,265
	Austrian
	41,479
	Norwegian
	49,210

### (28) Palladium-Silver

United States	2,001,017
2,143,217	1,999,866
2,138,599	1,999,864
2,132,116	1,965,012
2,129,728	1,963,085
2,123,330	1,962,859
2,095,890	1,935,897
2,070,271	1,930,119
2,058,857	1,924,097
2,050,077	1,913,423
2,050,040	1,229,037
2,048,648	
2,048,647	British
2,038,783	466,972
	452,401
	451,101

## SECTION 2. ALLOYS (Continued)

## (28) Continued

444,754	644,623
354,239	632,284
354,216	628,572
157,884	622,580
French	611,709
	610,599
	585,545
	551,798
	755,880
Austrian	154,006
	152,133
	141,479
	138,375
	43,934
German	Italian
	318,102
	Hungarian
	109,226

## (29) Phosphorus-Silver

United States	1,921,417
2,144,279	1,921,416
2,125,228	1,899,873
2,095,820	1,820,903
2,048,648	British
2,048,647	466,972
2,019,984	452,401
1,921,418	377,097

## (30) Platinum-Silver

United States	French	801,005
2,138,599		777,839
2,129,728		746,755
2,129,721		43,121
2,058,857	German	671,223
2,050,040		652,142
2,001,017		632,284
1,999,866		626,084
1,999,864		551,798
1,962,859		548,549
1,892,490		145,746
1,321,170	British	138,375
485,977		109,226
451,101		360,184
444,754		
379,485		
157,884		

## (33) Rhodium-Silver

United States	Canadian
2,143,217	343,808

## (35) Silicon-Silver

United States	German
2,052,143	588,187
2,052,142	541,105
1,986,209	496,349
1,970,319	Italian
1,970,318	328,640
1,792,580	Swiss
1,720,894	163,006
1,643,304	Austrian
French	122,706
747,789	Danish
	48,769

## (39) Tellurium-Silver

British	496,210
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## (40) Thallium-Silver

United States	German
1,899,465	595,851
1,863,612	496,348
British	494,153
297,665	

## (41) Thorium-Silver

United States	2,151,567
1,863,612	

## (42) Tin-Silver

United States	410,683
2,154,068	401,527
2,141,201	301,041
2,136,919	280,023
2,136,918	224,836
2,096,014	221,770
2,088,052	198,222
2,052,143	173,268
2,052,142	171,607
2,050,040	French
2,048,648	812,672
2,046,702	739,035
2,024,545	German
1,970,319	659,658
1,970,318	652,572
1,969,019	628,572
1,969,018	601,328
1,963,085	575,926
1,952,083	458,238
1,952,082	496,348
1,921,416	601,328
1,888,188	Canadian
1,863,612	353,526
1,843,304	315,801
1,826,925	268,129
1,826,038	Japanese
1,614,752	102,000
1,612,782	100,093
1,574,714	99,246
1,565,115	Italian
1,222,158	328,640
British	327,870
496,763	298,574
485,977	Swiss
477,721	182,772
474,716	155,832
456,018	Danish
440,480	32,989
440,450	

## (43) Titanium-Silver

United States	1,023,332
1,986,210	1,022,600
1,025,426	French
1,024,476	747,787

## (44) Tungsten-Silver

United States	437,713
2,131,994	416,683
2,057,604	399,695
1,984,203	French
1,574,714	802,263
British	792,568
456,018	German
449,847	643,567
444,396	

## (45) Vanadium-Silver

United States	British
1,574,714	171,607

## (46) Zinc-Silver

United States	440,450
2,141,157	410,683
2,141,156	402,640
2,138,638	355,422
2,138,637	280,073
2,083,052	259,108
2,058,857	209,975
2,053,662	French
2,052,143	812,672
2,052,142	761,496
2,050,040	755,880
2,045,138	746,755
2,042,155	739,035
2,041,381	728,230
2,024,545	706,312
2,019,984	632,368
2,001,639	145,056
1,970,319	43,934
1,970,318	43,121
1,969,019	German
1,963,085	671,223
1,947,938	659,658
1,941,039	628,572
1,930,119	613,511
1,924,097	601,328
1,921,760	596,023
1,921,418	551,798
1,921,417	548,238
1,921,416	496,348
1,899,873	492,779
1,899,701	Canadian
1,888,188	353,526
1,863,612	276,493
1,789,854	Japanese
1,778,276	110,779
1,731,213	102,000
1,731,212	91,104
1,731,211	Austrian
1,731,210	152,133
1,614,752	138,375
1,580,444	Indian
1,580,443	22,764
1,455,531	Australian
1,375,552	14,468
1,222,158	Hungarian
British	109,226
471,798	Russian
464,678	25,595
464,030	Swiss
461,845	155,832
441,754	
440,480	

## (47) Zirconium-Silver

United States	French
2,026,209	771,176
British	German
440,480	643,568
440,450	623,845
	623,844

## (48) Miscellaneous

## (48a) Osmium-Silver

United States	1,248,621
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## (48b) Rhenium-Silver

British	385,859
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## (48c) Tantalum-Silver

British	German
456,018	643,567
French	596,023
792,568	

## SECTION 3. BRAZING ALLOYS AND SOLDERS

<b>United States</b>	2,059,497	1,829,903	487,596	435,070	<b>French</b>
2,186,117	2,049,771	1,717,250	487,178	434,192	817,124
2,167,678	2,045,138	1,699,761	486,256	431,584	812,672
2,163,224	2,045,080	1,651,662	485,513	415,181	810,388
2,162,627	2,032,926	1,641,745	485,356	414,213	797,422
2,161,597	2,030,476	1,565,115	483,555	402,640	796,352
2,156,331	2,021,828	1,483,327	483,156	377,097	789,974
2,148,040	2,019,984	1,472,781	479,084	171,607	739,035
2,146,630	2,015,345	1,466,061	475,878	<b>German</b>	<b>Italian</b>
2,145,651	2,014,083	1,415,925	474,716	660,114	344,159
2,140,531	2,003,467	1,396,495	471,798	652,572	327,870
2,138,638	2,001,639	1,375,552	471,495	601,328	327,824
2,138,637	2,000,692	1,301,633	471,202	588,187	298,571
2,138,088	1,993,490	1,263,656	470,323	584,172	<b>Swedish</b>
2,136,496	1,968,841	1,222,158	468,049	355,906	87,399
2,134,366	1,947,938	1,215,138	467,375	202,295	<b>Australian</b>
2,125,228	1,921,418	1,181,742	467,259	<b>Swiss</b>	14,468
2,099,582	1,921,417	1,109,658	467,001	182,772	<b>Japanese</b>
2,094,483	1,921,416	1,103,482	466,049	102,522	102,000
2,094,482	1,899,873	<b>British</b>	460,113	155,533	76,991
2,087,716	1,899,701		454,070		
2,084,928	1,875,911	506,432	451,495		
2,073,371	1,835,965	492,088			

## SECTION 4. BEARINGS

<b>United States</b>	2,102,998	2,006,859	488,590	433,653	<b>French</b>
2,141,201	2,101,759	1,986,209	472,428	271,293	788,117
2,136,655	2,100,314	<b>British</b>	472,248	<b>German</b>	
2,134,306	2,096,014	502,229	458,324	667,121	
2,131,994	2,055,740	496,763	436,633	661,821	

## SECTION 5. ELECTRODEPOSITION

<b>United States</b>	1,982,774	1,720,215	467,838	<b>German</b>	806,917
2,136,496	1,981,920	1,712,244	467,190	660,114	798,343
2,136,024	1,981,215	1,646,842	467,019	657,365	797,485
2,131,994	1,971,761	1,579,819	467,001	654,357	789,074
2,126,633	1,970,950	1,548,432	466,949	652,451	767,656
2,126,386	1,959,531	1,545,942	460,890	645,129	765,017
2,113,997	1,954,316	1,545,941	459,545	644,602	738,450
2,113,517	1,949,781	1,538,944	459,231	642,665	737,661
2,110,792	1,949,131	1,527,734	454,017	641,168	737,433
2,108,700	1,947,180	1,523,015	451,703	634,480	732,279
2,105,352	1,941,376	1,515,658	451,088	631,534	712,431
2,100,214	1,934,730	1,501,420	450,979	630,934	704,663
2,094,784	1,921,941	1,501,049	450,740	627,559	668,800
2,091,259	1,908,222	1,431,113	449,958	627,264	663,173
2,077,634	1,906,179	1,416,929	443,954	626,996	649,387
2,075,477	1,906,178	1,243,041	443,428	621,489	484,592
2,073,371	1,904,241	1,219,466	440,938	611,258	440,205
2,067,507	1,903,860	1,208,507	440,045	608,268	<b>Canadian</b>
2,065,530	1,901,531	1,133,019	432,242	607,447	376,287
2,060,530	1,898,618	1,037,469	427,719	606,751	366,938
2,047,302	1,894,670	799,218	416,736	603,910	343,808
2,043,966	1,894,669	<b>British</b>	414,186	603,678	338,197
2,032,912	1,894,151	502,220	413,720	595,205	296,523
2,031,113	1,892,051	501,379	408,244	587,924	291,827
2,027,358	1,866,699	494,379	374,003	583,023	<b>Austrian</b>
2,025,528	1,857,664	493,485	372,631	582,633	152,133
2,024,150	1,857,507	492,036	371,229	564,088	127,778
2,023,512	1,851,219	491,173	367,941	548,238	
2,010,805	1,850,997	490,232	364,711	546,100	
2,008,282	1,846,733	485,977	341,704	535,294	34,079
2,003,467	1,829,938	485,905	338,383	519,268	33,135
1,997,166	1,782,002	485,526	333,462	502,532	<b>Hungarian</b>
1,997,165	1,779,457	484,447	333,246	492,022	119,142
1,995,225	1,779,435	476,375	315,460	483,481	<b>Italian</b>
1,993,623	1,759,493	475,588	173,268	309,187	<b>Japanese</b>
1,991,995	1,758,293	472,859	158,460	<b>French</b>	113,765
1,988,012	1,740,291	469,689	102,328	824,356	<b>Belgian</b>
1,984,225	1,720,216	469,681		817,545	421,919



## SECTION 6. SILVERING PROCESSES

United States	2,070,321	1,941,438	494,559	327,476	French
2,183,202	2,067,907	1,935,520	494,379	296,905	846,557
2,171,086	2,064,060	1,922,387	491,422		846,105
2,164,332	2,063,034	1,885,238	491,173	660,114	824,355
2,153,786	2,062,225	1,828,938	490,537	611,258	785,270
2,146,025	2,060,530	1,724,204	490,159	602,786	651,300
2,145,732	2,041,667	1,648,504	486,639	594,011	482,895
2,144,673	2,038,372	1,593,998	485,977	590,169	
2,144,044	2,030,476	1,583,268	485,526	587,353	159,419
2,143,723	2,028,853	1,574,544	461,275	587,169	129,233
2,142,104	2,023,422	1,324,090	454,937	585,914	Austrian
2,140,131	2,017,367	1,263,656	454,839	561,857	136,376
2,136,496	2,010,805	1,208,507	443,954	535,294	Belgian
2,136,024	2,000,310	1,037,469	440,045	502,532	425,220
2,135,873	1,997,625	905,229	432,587		306,305
2,135,480	1,994,633	799,218	432,242	110,936	384,610
2,120,203	1,994,112	581,775	432,242	110,744	382,562
2,113,977	1,989,764	526,147	414,186	110,268	Italian
2,105,440	1,988,012		378,874		281,520
2,103,538	1,982,774	515,148	376,122	Russian	Czechoslovakian
2,095,781	1,977,639	503,034	375,168	34,079	
2,079,784	1,977,625	497,240	361,409	358,904	37,900
2,077,387	1,942,686	496,716	343,309	348,131	

## SECTION 7. ELECTRICAL APPLICATIONS

a. Contacts and Welding Electrodes		a. Continued		b. Photoelectric and Electronic Applications	
United States	2,073,371	1,774,689	450,382	United States	464,105
2,187,379	2,073,371	1,771,997	450,274	2,178,238	459,539
2,187,378	2,070,271	1,732,839	444,445	2,178,233	459,231
2,187,377	2,061,624	1,658,713	427,719	2,159,755	459,146
2,186,245	2,058,857	1,651,662	416,684	2,151,567	458,586
2,179,960	2,057,604	1,605,432	416,683	2,128,582	456,629
2,178,508	2,053,662	1,590,091	412,074	2,123,024	454,937
2,177,288	2,049,771	1,561,247	399,695	2,103,267	451,839
2,175,899	2,049,500	1,538,246	361,041	2,102,760	450,274
2,171,697	2,048,648	1,436,844	354,239	2,095,781	443,395
2,170,431	2,045,647	1,395,269	354,216	2,078,447	441,639
2,169,592	2,047,302	1,362,455	323,124	2,077,634	435,169
2,169,189	2,046,702	1,358,908	224,826	2,077,633	428,680
2,166,248	2,046,380	1,357,272	221,770	2,077,442	426,205
2,165,481	2,046,056	1,346,192		2,073,522	424,195
2,162,380	2,045,138	1,321,170	French	2,066,878	416,703
2,162,062	2,037,447	1,296,938	830,258	2,060,977	335,587
2,161,576	2,037,446	1,229,960	823,238	2,049,472	French
2,161,575	2,033,710	1,229,037	808,129	2,047,731	817,545
2,161,574	2,033,709	1,223,322	807,786	2,045,369	810,432
2,161,254	2,032,926	1,215,138	792,508	2,045,637	808,840
2,161,253	2,032,912	1,181,742	767,056	1,998,334	799,097
2,159,763	2,026,209	1,166,129	46,598	1,997,479	788,697
2,157,933	2,020,949	1,101,534	German	1,988,525	773,946
2,154,068	2,003,467	937,285	652,142	1,985,006	German
2,151,905	2,001,134	937,284	649,958		649,691
2,146,722	1,999,866		643,567	492,036	Canadian
2,143,914	1,999,864	514,209	595,851	491,422	354,829
2,141,114	1,998,334	506,432	585,947	491,292	Austrian
2,141,113	1,990,783	503,752	Canadian	488,644	146,769
2,138,509	1,986,224	501,379	351,470	478,071	Danish
2,137,617	1,986,210	496,033	315,801	478,266	51,100
2,136,919	1,986,209	494,956	259,845	475,059	Russian
2,136,918	1,984,203	471,538	145,807	474,616	45,539
2,136,915	1,982,812	469,596	145,746	472,064	34,079
2,132,116	1,978,516	486,987	143,940	471,359	Swedish
2,131,994	1,970,084	467,838	127,778	468,333	82,257
2,131,104	1,940,962	467,162		465,763	
2,126,693	1,935,897	466,654	Swiss		
2,126,386	1,932,678	465,923	181,867		
2,123,330	1,928,429	463,357	Japanese		
2,119,965	1,913,423	462,442	101,632		
2,116,252	1,891,495	456,018	36,520		
Re-issue	1,883,650	452,411	Russian		
20,638	1,882,114	451,845	45,339		
2,099,551	1,860,795	450,619			
2,096,924	1,848,438				
2,094,754	1,822,682				
2,091,259	1,802,718				
2,080,811	1,776,276				

## c. Miscellaneous

Batteries, Insoluble Anodes, Resistors, etc.

United States	2,075,492
2,144,673	2,068,557
2,131,478	2,047,302
2,091,259	2,003,467
2,082,102	1,851,219

SECTION 7. ELECTRICAL APPLICATIONS (*Continued*)

<i>Continued</i>		<i>c. Continued</i>			<i>Continued</i>	
1,838,130	467,190	423,195	335,587	French	Austrian	
1,750,493	460,895	416,083	315,556		143,949	
1,740,291	454,448	415,912		German	Italian	293,506
	440,847	406,086	634,489	Norwegian		
505,949	444,396	392,859	568,032		57,320	
496,033						

## SECTION 8. USE OF SILVER IN CATALYSTS

United States	2,061,617	2,010,337	British	430,234	French	
2,185,007	2,050,788	2,005,645	469,434		825,983	
2,164,826	2,042,220	1,998,878	466,416	427,631	802,542	
2,128,032	2,041,184	1,976,790	402,487	425,927	794,751	
2,125,333	2,033,161	1,968,552	453,419	426,550	780,050	
2,124,331	2,027,378	1,955,211	451,130	237,030	771,650	
2,111,203	2,021,885	1,951,280	450,449	156,245	45,761	
2,096,924	2,019,419	1,945,267	449,783	156,244	45,301	
2,092,449	2,018,680	1,824,896	447,973	German	35,381	
2,063,365	2,015,751	1,888,995	444,186	632,825		
2,061,620	2,015,094	1,357,000	431,966	627,676		

## SECTION 9. CORROSION

<i>a. Corrosion-Resistant</i>		<i>a. Continued</i>		<i>a. Continued</i>	
United States	1,994,112	1,847,941	297,065	Canadian	Italian
2,172,428	1,970,319	1,816,961	257,473	344,789	318,102
2,172,427	1,970,318	1,773,702	German	Japanese	
2,172,422	1,969,705	1,758,293	592,710	99,246	
2,172,421	1,969,019	1,757,508	548,238		
2,172,388	1,969,018	1,740,291	543,627		
2,150,914	1,952,083	1,720,894	494,153		
2,144,279	1,952,082	1,720,216	490,248	United States	1,766,646
2,141,201	1,935,897	1,719,365	463,876	2,136,483	1,758,293
2,124,721	1,934,730	1,719,365	460,378	2,134,306	1,628,010
2,052,143	1,917,378	1,643,304	97,425	2,117,657	1,564,786
2,052,142	1,913,423	1,628,673	60,255	2,051,697	1,561,650
2,040,093	1,896,410	1,614,752	French	2,017,029	1,560,659
2,033,161	1,888,188	1,555,531	780,050	2,003,333	German
2,031,113	1,863,645	1,191,890	45,761	1,995,225	572,324
2,015,345	1,863,612	81,575	43,934	1,949,781	548,238
2,003,333	1,859,413	British	35,831	1,947,180	Canadian
		374,003		1,846,733	301,723

*b. Tarnish Prevention*

United States	1,766,646
2,136,483	1,758,293
2,134,306	1,628,010
2,117,657	1,564,786
2,051,697	1,561,650
2,017,029	1,560,659
2,003,333	German
1,995,225	572,324
1,949,781	548,238
1,947,180	Canadian
1,846,733	301,723

## SECTION 10. STERILIZATION

United States	1,685,204	425,696	3,461	317,185	690,874
2,154,052	1,642,089	422,948	2,020	309,187	684,642
2,121,875	1,557,235	421,692	German	French	537,890
2,109,151	1,537,234	415,213	661,311	819,152	
2,105,835	1,473,331	412,782	653,362	811,041	Swiss
2,086,324	1,227,527	410,838	632,825	810,280	171,731
2,066,710	1,202,557	395,570	630,677	790,803	169,716
2,066,271	1,197,557	355,086	629,680	784,959	98,184
2,061,467	1,191,572	353,686	624,061	783,767	Belgian
2,046,457		353,409	618,374	782,509	396,748
2,042,534	476,376	351,992	617,153	781,685	393,984
2,040,806	474,614	340,218	613,120	781,018	Russian
2,036,949	463,794	325,796	609,336	780,773	50,105
2,028,072	457,785	306,547	598,069	777,588	46,481
2,018,916	457,783	304,466	593,363	771,194	Austrian
2,008,131	435,543	300,898	593,069	769,281	145,598
1,988,246	432,101	293,385	592,090	767,245	144,019
1,955,211	431,872	279,085	556,137	765,017	Canadian
1,883,987	431,656	274,909	517,105	764,660	313,197
1,883,420	430,635	202,143	422,903	760,799	288,978
1,850,594	430,090	180,973	419,657	757,173	245,403
1,813,064	429,270	157,280	336,989	756,351	Swedish
1,812,105	428,853	29,049	329,189	692,364	82,551
1,758,651	428,764	21,521	325,505		

## SECTION 11. MISCELLANEOUS

## a. Photographic Applications and Recovery

United States	1,959,531
2,194,056	1,954,951
2,184,022	1,954,816
2,183,661	1,905,467
2,178,612	1,857,507
2,177,257	1,527,942
2,171,911	1,448,475
2,166,736	1,425,935
2,165,338	
2,162,936	British 499,201
2,156,626	476,985
2,155,475	427,464
2,154,895	390,664
2,153,930	363,631
2,153,928	331,006
2,147,672	German 655,190
2,144,932	639,394
2,143,995	633,685
2,110,930	625,333
2,107,094	621,677
2,096,011	498,491
2,073,664	
2,073,662	French 834,009
2,045,080	736,241
2,016,718	732,915
1,997,479	Canadian 305,246
1,994,633	
1,962,306	

## b. Silverware

United States	1,859,413
2,126,737	1,823,938
2,061,624	1,779,809
2,051,697	1,757,507
2,003,333	1,720,894
1,999,866	1,720,275
1,999,864	1,720,216
1,969,019	1,720,215
1,969,018	1,719,265
1,952,083	1,643,304
1,952,082	1,628,673
1,949,781	1,590,091

## b. Continued

	1,564,786	German	502,532
	1,561,650		
	1,560,659	Canadian	343,020
	1,538,944		301,723
	1,501,049		
British		Danish	48,760
	494,956		
	485,905	Japanese	110,779
	186,381		
French		Swiss	155,832
	760,388		
	632,368		

## c. Jewelry and Decorative Applications

United States	1,580,444
2,141,157	1,580,443
2,141,156	1,579,819
2,138,088	1,561,650
2,132,116	1,206,938
2,129,728	1,283,264
2,129,721	1,149,850
2,126,737	1,075,642
2,101,065	1,025,426
2,095,820	1,024,476
2,075,477	808,453
2,062,226	25,206
2,042,155	
2,041,381	British 485,513
2,033,783	483,565
2,000,310	471,495
1,987,452	468,049
1,987,451	466,049
1,984,225	461,405
1,977,625	461,101
1,965,012	450,740
1,917,378	225,200
1,906,689	186,381
1,888,188	152,277
1,731,213	
1,731,212	French 811,305
1,731,211	801,005
1,731,210	777,839
1,720,215	772,280

## c. Continued

	712,507	Italian	344,159
	699,068		
German	43,934	Belgian	360,184
		Austrian	141,470
	659,155	Japanese	91,104
	643,568		
	624,927		
	595,205		

## d. Dental Applications

United States	British
2,172,512	452,401
2,143,950	450,397
2,123,330	444,754
2,098,879	405,862
2,083,052	359,014
2,050,077	354,230
2,050,040	German 671,223
2,018,648	669,905
2,018,647	659,658
2,039,880	643,568
2,025,759	626,615
2,024,545	626,084
1,987,452	575,926
1,987,451	551,798
1,965,012	499,677
1,963,085	474,887
1,962,859	
1,936,333	French 801,005
1,935,897	767,656
1,930,119	754,065
1,924,097	746,755
1,913,423	688,967
1,892,490	
1,612,782	Canadian 353,526
1,574,714	351,479
1,574,514	
1,339,009	Austrian 154,006
1,283,264	152,133
1,164,997	141,479
475,382	
104,879	Russian 29,594
	25,595

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Note: Alloys are listed under their chemical symbols; for example, tin-silver appears as Sn-Ag, gold-silver as Au-Ag, etc.

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